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Article

Rational Design and Assembly of a New Series of Cyanide-Bridged $\mathrm{Fe^{III}{-}Mn^{II}}$ One-Dimensional Single Chain Complexes: Synthesis, Crystal Structures, and Magnetic Properties

Daopeng Zhang,[†,‡] Hailong Wang,[†,‡] Yuting Chen,[‡] Zhong-Hai Ni,[*,‡] Laijin Tian,[‡] and Jianzhuang Jiang[*,†,‡]

[†] *Department of Chemistry, University of Science and Technology Beijing, Beijing 100083, China, and*
[‡] *Department of Chemistry, Shandong University, Jinan 250100, China*

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Two mononuclear seven-coordinated macrocycle manganese(II) compounds and three dicyanide-containing precursors have been employed as building blocks to assemble cyanide-bridged heterobimetallic complexes, resulting in five new cyanide-bridged single chain complexes $\{[\mathrm{Mn(L^1)}][\mathrm{Fe(bpb)(CN)_2}]\}\mathrm{ClO_4}\cdot 0.5\mathrm{H_2O}$ (**2**), $\{[\mathrm{Mn(L^2)}][\mathrm{Fe(bpb)(CN)_2}]\}\mathrm{ClO_4}\cdot 0.5\mathrm{H_2O}$ (**3**), $\{[\mathrm{Mn(L^1)}][\mathrm{Fe(bpClb)(CN)_2}]\}\mathrm{ClO_4}\cdot \mathrm{H_2O}$ (**4**), $\{[\mathrm{Mn(L^2)}][\mathrm{Fe(bpClb)(CN)_2}]\}\mathrm{ClO_4}\cdot 0.5\mathrm{H_2O}$ (**5**), and $\{[\mathrm{Mn(L^1)}][\mathrm{Fe(bpdBrb)(CN)_2}]\}\mathrm{ClO_4}\cdot \mathrm{H_2O}$ (**6**). Single X-ray diffraction analysis reveals their one-dimensional (1D) single cyanide-bridged cationic polymeric chain structure consisting of alternating units of $[\mathrm{Mn(L)}]^{2+}$ ($\mathrm{L} = \mathrm{L^1}$ or $\mathrm{L^2}$) and $[\mathrm{Fe(L')(CN)_2}]^-$ ($\mathrm{L'} = \mathrm{bpb^{2-}}$, $\mathrm{bpClb^{2-}}$ or $\mathrm{bpdBrb^{2-}}$) with free $\mathrm{ClO_4}^-$ as balanced anion. Similar to the mononuclear macrocyclic manganese(II) precursor $\{[\mathrm{Mn(L^2)(H_2O)Cl}]\mathrm{ClO_4}\}\cdot \mathrm{CH_3OH}$ (**1**), the coordination geometry of manganese(II) ion in all the 1D complexes is a slightly distorted pentagonal-bipyrimidal with two cyanide nitrogen atoms at the trans positions and $\mathrm{N_5}$ or $\mathrm{N_3O_2}$ coordinating mode at the equatorial plane from ligand $\mathrm{L^1}$ or $\mathrm{L^2}$. Investigation of the magnetic properties of these five 1D single chain cyanide-bridged $\mathrm{Fe^{III}{-}Mn^{II}}$ complexes reveals the antiferromagnetic magnetic coupling between neighboring Fe(III) and Mn(II) ions through the bridging cyanide group. A best-fit to the magnetic susceptibilities of these complexes based on the 1D alternating chain model leads to the magnetic coupling constants $J_1 = -1.16(2)$ and $J_2 = -0.10(3)\ \mathrm{cm^{-1}}$ for **2**, $J_1 = -3.10(1)$ and $J_2 = -0.25(1)\ \mathrm{cm^{-1}}$ for **3**, $J_1 = -1.10(1)$ and $J_2 = -0.139(8)\ \mathrm{cm^{-1}}$ for **4**, $J_1 = -1.99(6)$ and $J_2 = -0.57(1)\ \mathrm{cm^{-1}}$ for **5**, and $J_1 = -1.23(1)$ and $J_2 = -0.13(5)\ \mathrm{cm^{-1}}$ for **6**, respectively. This work will provide valuable information for the rational design and synthesis of low-dimensional, in particular, single chain, cyanide-bridged magnetic complexes.

Introduction

In the past three decades, the design and synthesis of molecular magnetic materials has attracted extensive interest in several scientific fields including chemistry, physics, materials, and biology. As one of the most excellent building blocks for the rational construction of molecular functional materials, about twenty cyanide-containing precursors with or without peripheral organic ligands have been employed to synthesize cyanide-bridged magnetic compounds with diversified molecular topological structures and interesting magnetic properties such as high-T_c magnets,[1] spin crossover materials,[2] photomagnetic materials,[3] and

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*To whom correspondence should be addressed. E-mail: jzjiang@sdu.edu.cn.

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single-molecule magnets (SMMs),[4] as well as single-chain magnets (SCMs).[5]

Very recently, low-dimensional cyanide-bridged complexes[6−17] attracted much attention for the purpose of clearly elucidating magneto-structural correlations and preparing interesting molecular materials such as SMMs and SCMs. To synthesize low-dimensional cyanide-bridged complexes with desirable molecular structure, several factors such as the number and position of cyanide group, the number and nature of charge of cyanide-containing building blocks, and the steric effect of reactants must be taken into account. Although many cyanide-bridged low-dimensional magnetic compounds have been synthesized thus far, it still remains a great challenge for chemists to rationally design and synthesize this type of cyanide-bridged compounds.

With this idea in mind, we have focused our interest on the controllable synthesis of one-dimensional (1D) cyanide-bridged chain complexes through rational design and selection of cyanide-containing building blocks with relative large equatorial in-plane ligands and two trans cyanide groups, which have been testified as good candidates for assembling low dimensional cyanide-bridged heterometallic complexes.[4f,18] On the other hand, the ancillary ligands attached to the counterpart assembling cations also play a crucial role in influencing the structure of resulting complexes. Macrocyclic ligands, which are usually coordinated to the equatorial plane of metal ions, with two trans replaceable sites being occupied by other ligands, can be used as good ancillary ligands to effectively lower the dimensionality of the complex formed. In this paper, we describe the design, synthesis, crystal structures, and magnetic properties of a new series of five cyanide-bridged 1D $Fe^{III}-Mn^{II}$ heterometallic complexes assembled from three appropriate dicyanideiron (III) and two seven-coordinated manganese(II) building blocks with 15-membered macrocyclic as ancillary ligands, Scheme 1. To the best of our knowledge, cyanide-bridged $Fe^{III}-Mn^{II}$ complexes with perfect single chain structure remain very rare although several examples with double zigzag chain structure were structurally characterized.[5d,7a,16b,19−21]

Experimental Section

Elemental analyses of carbon, hydrogen, and nitrogen were carried out with an Elementary Vario El. The infrared spectroscopy on KBr pellets was performed on a Magna-IR 750 spectrophotometer in the 4000−400 cm^{-1} region. Variable-temperature magnetic susceptibility and field dependence magnetization measurements were performed on a Quantum Design MPMS SQUID magnetometer. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's tables).

General Procedures and Materials. All the reactions were carried out under an air atmosphere, and all chemicals and solvents used were reagent grade without further purification. $K[Fe^{III}(bpb)(CN)_2]$ [bpb^{2-} = 1,2-bis(pyridine-2-carboxamido) benzenate] was synthesized as described in literature.[22] The two analogous complexes $K[Fe^{III}(bpClb)(CN)_2]$ [$bpClb^{2-}$ = 1,2-bis(pyridine-2-carboxamido)-4-chorobenzenate] and $K[Fe^{III}(bpdBrb)(CN)_2]$ [$bpdBrb^{2-}$ = 1,2-bis(pyridine-2-carboxamido)-4,5-dibromobenzenate] were similarly prepared. The two manganese precursors were prepared using a slightly modified method reported previously.[23,24]

Caution! *KCN is hypertoxic and hazardous. Perchlorate salts of metal complexes with organic ligands are potentially explosive. They should be handled in small quantities with care.*

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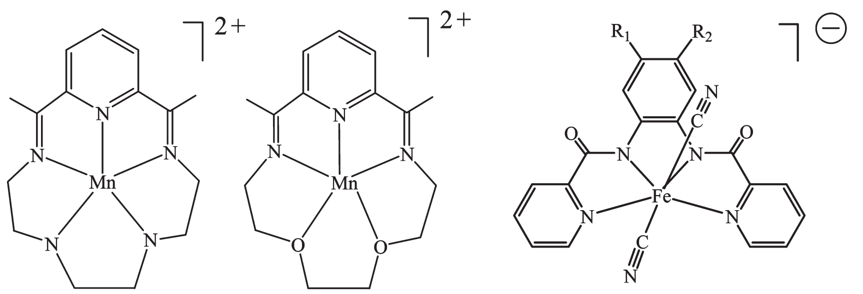
Scheme 1



$[Mn(L^1)]^{2+}$ $[Mn(L^2)]^{2+}$ *trans*-$[Fe^{III}(L')(CN)_2]^-$ ($L' = bpb^{2-}$, $R_1 = R_2 = H$; $bpClb^{2-}$, $R_1 = H$, $R_2 = Cl$; $bpdBrb^{2-}$, $R_1 = R_2 = Br$)

Synthesis of Macrocyclic Manganese(II) Compounds $[Mn(L^1)(H_2O)Cl]ClO_4$ and $\{[Mn(L^2)(H_2O)Cl]ClO_4\}\cdot CH_3OH$ (1). Ethanol solution containing 2,6-diacetylpyridine (1.64 g, 10 mmol) was mixed with another ethanol solution containing $MnCl_2\cdot 4H_2O$ (2.0 g, 10 mmol) under stirring; then the ethanol solution of 3,6-diazaoctano-1,8-diamine (1.47 g, 10 mmol) or 3,6-dioxaoctano-1,8-diamine (1.49 g, 10 mmol) was added slowly. The mixture was stirred for 5 h with the temperature maintaining at 60 °C, then $NaClO_4\cdot H_2O$ (1.41 g, 10 mmol) was added. The resulting mixture was stirred for about 0.5 h at room temperature and filtered to remove insoluble material. After the solvent was partially removed, excessive amount of diethyl ether was added to precipitate the product. The orange solid formed was isolated by filtration, washed with diethyl ether, and dried in air. Yield: 55−60%. For $\{[Mn(L^2)(H_2O)Cl]ClO_4\}\cdot CH_3OH$ **(1)**, crystals suitable for X-ray diffraction were obtained from its methanol solution layered with diethyl ether. Anal. Calcd for $C_{16}H_{27}C_{12}MnN_3O_8$: C, 37.30; H, 5.28; N, 8.16. Found: C, 37.22; H, 5.31; N, 8.32.

Synthesis of Complexes 2−6. All the five target complexes were prepared using one similar procedure, therefore only the synthesis of **2** was detailed as a typical representative. To a solution of $[Mn(L^1)(H_2O)Cl]ClO_4$ (48.1 mg, 0.10 mmol) in methanol (10 mL), $K[Fe(bpb)(CN)_2]$ (46.5 mg, 0.10 mmol) dissolved in methanol/water (4:1, v:v) (10 mL) was carefully added. The resulting mixture was filtered at once, and the filtrate kept undisturbed at room temperature. After 1 week, brown-black block crystals were collected by filtration with the yield of 49.5 mg, 57.5%. Anal. Calcd for $C_{35}H_{36}ClFeMnN_{11}O_{6.5}$: C, 48.83; H, 4.22; N, 17.90. Found: C, 48.88; H, 4.31; N, 17.81. Main IR bands (cm^{-1}): 2126 (s, $\nu C{\equiv}N$), 1617, 1623 (vs, $\nu C{=}N$), 1095 (vs, $\nu Cl{=}O$).

Complex **3**: Yield: 44.8 mg, 51.9%. Anal. Calcd for $C_{35}H_{34}ClFeMnN_9O_{8.5}$: C, 48.72; H, 3.97; N, 14.61. Found: C, 48.78; H, 4.01; N, 14.45. 2131 (s, $\nu C{\equiv}N$), 1619, 1625 (vs, $\nu C{=}N$), 1099 (vs, $\nu Cl{=}O$).

Complex **4**: Yield: 51.3 mg, 56.7%. Anal. Calcd for $C_{35}H_{36}Cl_2FeMnN_{11}O_7$: C, 46.48; H, 4.01; N, 17.04. Found: C, 46.54; H, 4.05; N, 16.95. 2130 (s, $\nu C{\equiv}N$), 1621, 1629 (vs, $\nu C{=}N$), 1100 (vs, $\nu Cl{=}O$).

Complex **5**: Yield: 62.1 mg, 69.2%. Anal. Calcd for $C_{35}H_{33}Cl_2FeMnN_9O_{8.5}$: C, 46.85; H, 3.71; N, 14.05. Found: C, 46.91; H, 3.75; N, 13.95. 2130 (s, $\nu C{\equiv}N$), 1615, 1624 (vs, $\nu C{=}N$), 1091 (vs, $\nu Cl{=}O$).

Complex **6**: Yield: 40.9 mg, 39.8%. Anal. Calcd for $C_{35}H_{35}Br_2ClFeMnN_{11}O_7$: C, 40.90; H, 3.43; N, 14.99. Found: C, 40.95; H, 3.45; N, 14.91. 2132 (s, $\nu C{\equiv}N$), 1623, 1635 (vs, $\nu C{=}N$), 1092 (vs, $\nu Cl{=}O$).

X-ray Data Collection and Structure Refinement. Single crystals of all the complexes for X-ray diffraction analysis with suitable dimensions were mounted on the glass rod, and the crystal data were collected on a Bruker SMART CCD diffractometer with a Mo Kα sealed tube (λ = 0.71073 Å) at 273 K, using a ω scan mode. The structures were solved by the direct method and expanded using Fourier difference techniques with the SHELXTL-97 program package. The non-hydrogen atoms were refined anisotropically, while hydrogen atoms were introduced as fixed contributors. All the non-hydrogen atoms except the disordered ones were refined with anisotropic displacement coefficients. For the disordered contents, the partially occupied atoms were refined isotropically. Hydrogen atoms were assigned isotropic displacement coefficients $U(H) = 1.2U(C)$ or $1.5U(C)$ and their coordinates were allowed to ride on their respective carbons using SHELXL97 except some of the H atoms of the solvent molecules. For these H atoms, they were refined isotropically with fixed U values and the DFIX command was used to rationalize the bond parameter. CCDC 722358, 722357, 722362, 722359, 722360, and 722361 for complexes **1**−**6** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Details of the crystal parameters, data collection, and refinement are summarized in Table 1.

Results and Discussion

Synthesis and General Characterization. As shown in Scheme 1, the 15-membered, pentadentate macrocycles L^1 and L^2 (L^1 = 3,6-diazaoctane-1,8-diamine, L^2 = 3,6-dioxaoctano-1,8-diamine) have been found to adopt a planar conformation, imposing a pentagonal-based geometry on the central metal ion with different electronic configuration, leading to the stabilization of seven-coordinated species. In contrast to other manganese(II) complexes with aliphatic amines, the two seven-coordinated Mn(II) species obtained by incorporating Mn(II) ion into these two macrocyclic ligands in the present work are very robust and can be handled in air and in aqueous solution without being oxidized. Because of the large steric effect coming from the macrocyclic ligand and the existence of two weakly bonded and replaceable ligands at the two *trans* positions, these two seven-coordinated Mn(II) compounds are some of the most excellent precursors for the design and synthesis of low-dimensional complexes.[23,25−27]

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Table 1. Crystallographic Data for Complexes **1**−**6**

	1	**2**	**3**	**4**	**5**	**6**
chemical formula	$C_{16}H_{27}Cl_2$ MnN_3O_8	$C_{35}H_{36}ClFe$ $MnN_{11}O_{6.5}$	$C_{35}H_{34}ClFe$ $MnN_9O_{8.5}$	$C_{35}H_{36}Cl_2Fe$- $MnN_{11}O_7$	$C_{35}H_{33}Cl_2Fe$- $MnN_9O_{8.5}$	$C_{35}H_{35}Br_2ClFe$- $MnN_{11}O_7$
Fw	515.25	860.99	862.95	904.44	897.39	1027.80
crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2(1)/c$	$C2/c$	$P2(1)/c$	$P2(1)/c$	$P2(1)/c$
a/Å	7.1991(6)	11.3896(3)	25.416(3)	11.453(3)	11.358(11)	11.936(5)
b/Å	11.6817(10)	17.8220(4)	19.276(3)	17.850(4)	17.665(18)	17.341(8)
c/Å	14.5535(11)	20.4585(4)	19.361(3)	20.519(4)	20.412(2)	20.443(9)
α/deg	69.3660(10)	90	90	90	90	90
β/deg	81.1560(10)	99.7460(10)	126.656(2)	99.453(4)	101.923(2)	97.908(9)
γ/deg	85.8990(10)	90	90	90	90	90
V/Å^3	1131.59(16)	4092.84(16)	7609.6(18)	4137.7(16)	4007.0(7)	4191(3)
Z	2	4	8	4	4	4
F(000)	534	1772	3544	1856	1836	2064
GOF	1.033	1.039	1.038	1.052	1.037	1.021
$R_1[I > 2\sigma(I)]$	0.0514	0.0702	0.0549	0.0786	0.0805	0.0785
wR_2 (all data)	0.1590	0.2289	0.1788	0.2477	0.2682	0.2142

Table 2. Selected Bond Lengths and Angles for Complexes **2**−**6**[a]

	2	**3**	**4**	**5**	**6**
Mn1−N1	2.260(4)	2.205(4)	2.276(8)	2.221(5)	2.276(8)
Mn1−N2	2.235(4)	2.212(4)	2.234(9)	2.243(5)	2.278(8)
Mn1−N7	2.268(6)	2.216(4)	2.237(14)	2.170(7)	2.197(17)
Mn1−N8	2.245(6)	2.254(4)	2.273(12)	2.155(10)	2.283(15)
Mn1−N9	2.323(7)	2.247(4)	2.316(11)	2.243(11)	2.346(14)
Mn1−N10/O3	2.355(7)	2.289(4)	2.343(13)	2.316(10)	2.443(16)
Mn1−N11/O4	2.326(6)	2.274(4)	2.368(15)	2.280(8)	2.31(2)
Fe1−C1	1.966(5)	1.958(5)	1.964(10)	1.965(6)	1.964(10)
Fe1−C2	1.960(4)	1.956(5)	1.964(11)	1.966(6)	1.934(10)
Fe1−N3	1.895(4)	1.895(3)	1.879(10)	1.870(7)	1.898(8)
Fe1−N4	1.891(4)	1.878(3)	1.897(9)	1.934(7)	1.858(8)
Fe1−N5	1.993(4)	2.007(3)	1.987(9)	2.005(5)	1.976(9)
Fe1−N6	2.000(4)	1.987(4)	2.034(10)	2.006(7)	2.000(8)
N1−Mn1−N2	177.04(16)	173.86(16)	176.7(3)	172.2(2)	174.4(3)
Mn1−C1−N1	162.2(4)	159.1(4)	163.3(7)	148.1(5)	166.8(8)
Mn1−C2#1−N2	154.6(4)	146.9(4)	155.0(8)	167.3(5)	153.2(8)
Fe1−N1−C1	175.6(4)	174.7(4)	174.1(8)	177.4(6)	172.0(9)
Fe1−N2#2−C2	173.9(5)	176.7(5)	174.8(8)	174.3(6)	175.3(9)

[a] **2**: #1: $x, -y+3/2, z-1/2$ #2: $x, -y+3/2, z+1/2$; **3**: #1: $-x+1/2, y-1/2, -z+3/2$ #2: $-x+1/2, y+1/2, -z+3/2$; **4**: #1: $x, -y+3/2, z-1/2$ #2: $x, -y+3/2, z+1/2$; **5**: #1: $x, -y+1/2, z-1/2$ #2: $x, -y+1/2, z+1/2$; **6**: #1: $x, -y+1/2, z-1/2$ #2: $x, -y+1/2, z+1/2$.

As suggested by recent work,[4f,18] dicyanide-containing iron complexes $[Fe(bpb)(CN)_2]^-$ with relative large planar equatorial pyridinecarboxamido ligand and two *trans* cyanide groups are good building blocks for synthesizing low-dimensional cyanide-bridged complexes. As a consequence, reaction of $[Fe(bpb)(CN)_2]^-$ with the above-mentioned macrocyclic manganese(II) precursors might result in complexes with expected 1D cyanide-bridged single chain structure because of the suitable steric effect of peripheral organic ligands, active reacting sites, and charge of these two building blocks. Indeed, reaction between $K[Fe(L')(CN)_2]$ and $[Mn(L)(H_2O)Cl]ClO_4$ with 1:1 molar ratio led to the isolation of five heterometallic cyanide-bridged complexes. As detailed below, all the five complexes exhibit an infinite 1D cyanide-bridged single cationic chain structure with free ClO_4^- groups as the counterpart anion. To prepare trinuclear neutral $Fe^{III}-Mn^{II}-Fe^{III}$ complexes, reaction between $K[Fe(L')(CN)_2]$ and $[Mn(L)(H_2O)Cl]ClO_4$ with 2:1 molar ratio was carried out. However, the products are just the same as obtained from the reaction in the molar ratio of 1:1. It is worth noting that complexes **2**, **4**, **5**, and **6** crystallize in the monoclinic $P2(1)/c$ group. However, compound **3** crystallizes in monoclinic $C2/c$ group probably because of the different number of independent units in the unit cell.[18c,28]

All the cyanide-bridged complexes have been characterized by IR spectra. In the IR spectra of complexes **2**−**6**, the broad single peak in the range of 2125−2135 cm^{-1} can be assigned to the bridging cyanide groups. Observation of a strong broad peak centered at about 1090 cm^{-1} suggests the presence of ClO_4^- anions.

Crystal Structures of Complexes 2−6. The selected bond lengths and angles for complexes **2**−**6** are given in Table 2. The labeling scheme for the crystal structure and supermolecular chain formed by hydrogen bonds of mononuclear compound **1** is shown in Figure 1. For **2** and **3**, their asymmetry cationic unit and 1D cationic chain structures are shown in Figures 2 and 3, respectively. For **4**, **5**, and **6**, their 1D cationic chain structures are given in Figure 4. The representative cell packing diagram for **2**, **4**, and **6** is depicted in Figure 5, and those for **3** and **5** are given in Supporting Information, Figure S1.

As can be found, complexes **2**−**6** possess 1D cationic single chain structure composed of repeated [-NC-Fe(L′)-CN-Mn(L)-] units with the positive charge balanced by ClO_4^- anions. In these five complexes, each $[Fe(L')(CN)_2]^-$ unit, acting as a bidentate ligand through its two cyanide groups, connects the Mn(II) ion of two independent macrocyclic manganese units. The Fe atom is coordinated by four N atoms of cyanide-containing precursor located in the equatorial plane and two C atoms of cyanide groups in *trans* position, forming a slightly distorted octahedral geometry. The Fe−N bond length is in the range of 1.858(8)−2.000(8) Å for these complexes. The $Fe-C_{cyanide}$ bond length is distributed to the narrow range of 1.9134(10)−1.966(6) Å. As listed in Table 2, the bond angle of Fe−C≡N in the range of 172.0(9)−177.4(6)° clearly indicates that the three atoms are in a good linear configuration.

Similar to that in the mononuclear compound **1**, the Mn(II) ion in complexes **2**−**6** is seven-coordinated, forming a slightly distorted pentagonal-bipyrimidal coordination

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geometry, in which the five equatorial positions are occupied by the N_5 or N_3O_2 unit coming from the macrocyclic ligand and two axial ones coordinated by two N atoms of cyanide groups. The distances between Mn ion and equatorial N or O atoms, Table 2, are in good agreement with those found in its precursors compound **1** and $[Mn(L^1)(H_2O)_2]Cl_2$.[24] The average Mn−$N_{cyanide}$ bond lengths in all the five complexes are 2.307, 2.209, 2.255, 2.232, and 2.277 Å, respectively, consistent with the Mn−$N_{equatorial}$ bond lengths. As tabulated in Table 2, the bond angle of N1−Mn1−N2 spans a very narrow range of 172.2(2)−177.04(16)°, indicating the good linear configuration of these three atoms. However, the Mn−C≡N bond angle is somewhat bent. Careful inspection of the Mn−C≡N bond angles in these complexes reveals inconspicuous difference for the two angles. The angles of Mn1−N1−C1 and Mn1−C2#1−N2 (#1: the symmetry transformation used to generate equivalent atoms) are 162.2(4), 154.6(4), 163.3(7), 155.0(8), and 166.8(8), 153.2(8)° in complexes **2**, **4**, and **6**, while those in **3** and **5** are 159.1(4), 146.9(4), and 148.1(5), 167.3(5)°, respectively. The intramolecular Fe^{III}−Mn^{II} separation through bridging cyanide(s) in **2**−**6** is in the realm of 5.076−5.313 Å, while the shortest intermolecular metal−metal distance in the range of 7.754−8.171 Å is obviously longer than this value.

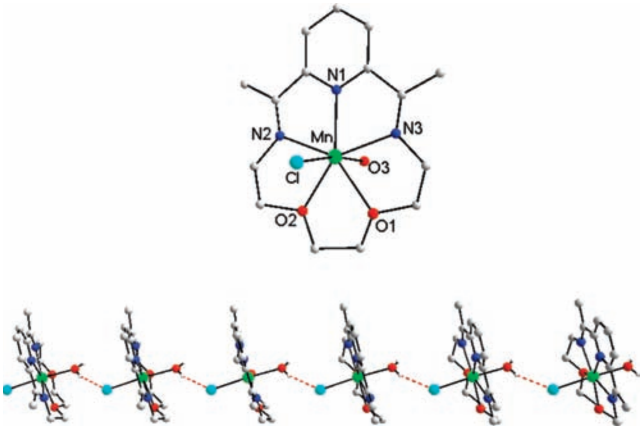


Figure 1. Crystal structure of compound **1** and its 1D chain supramolecular structure formed via hydrogen bonds. The free ClO_4^- group, solvent methanol molecule, and all the hydrogen atoms except those used to form hydrogen bond have been omitted for clarity.

Magnetic Properties of Complexes 2−6. The temperature dependence of magnetic susceptibilities was measured in the range of 2−300 K under the external magnetic field of 2000 Oe. The temperature dependence of the $\chi_m T$ product per $Fe^{III}Mn^{II}$ unit for complexes **2**−**6** is illustrated in Figure 6. The changing tendency of $\chi_m T$ for **2**, **4**, and **6** is very similar from one to another. The $\chi_m T$ value at room temperature is 4.54, 4.32, and 4.45 emu K mol^{-1} for **2**, **4**, and **6**, respectively, which is slightly lower than the spin only value of 4.75 emu K mol^{-1} for uncoupled Mn(II) ($S = 5/2$) and low spin Fe(III) ($S = 1/2$) based on $g = 2.00$. With decreasing the temperature, the $\chi_m T$ value decreases with a very low speed and attains the value of 4.38 emu K mol^{-1} for **2**, 4.18 for **4**, and 4.35 emu K mol^{-1} for **6** at about 50 K, respectively. After this, the $\chi_m T$ value starts to decrease with a high speed and reaches its lowest peak with the value about 3.06 emu K mol^{-1} for **2**, 3.09 for **4**, and 3.05 emu K mol^{-1} for **6** at 2 K.

For **3** and **5**, the changing tendency of $\chi_m T$ is similar to the above-mentioned three complexes from 300 K to about 8 K except that the $\chi_m T$ value decreases with a comparatively fast speed along with the temperature decreasing. The $\chi_m T$ value at room temperature is 4.55 and 4.58 emu K mol^{-1} for **3** and **5**, respectively, and reaches the lowest value of 3.16 for **3** and 3.75 emu K mol^{-1} for **5** with the temperature lowering to about 8 K. Different from **2**, **4**, and **6**, the $\chi_m T$ value begins to increase rapidly from this point

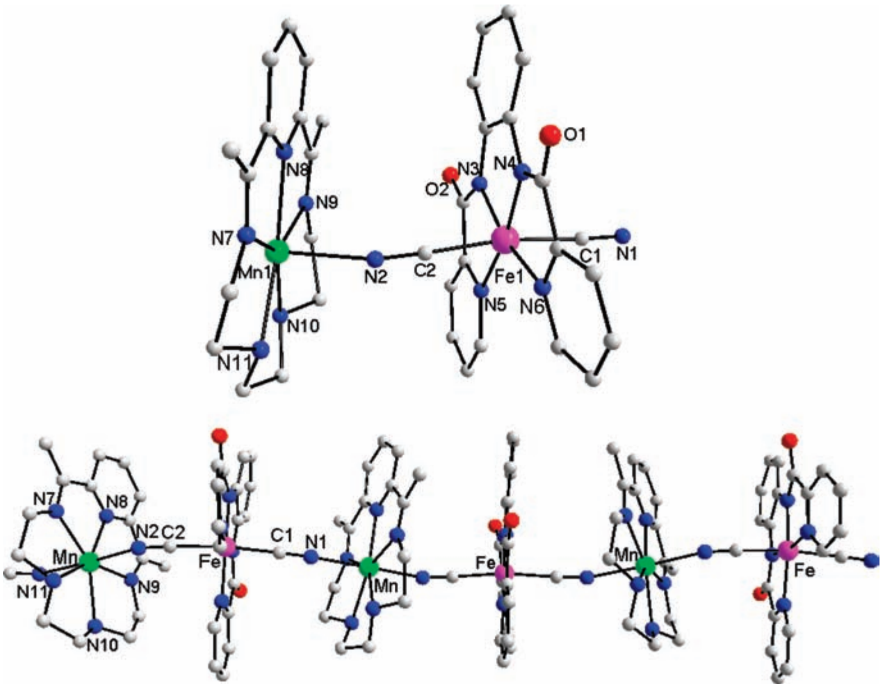


Figure 2. Asymmetry cationic unit and 1D cationic chain structure of complex **2**. All the hydrogen atoms, free ClO_4^-, and solvent water molecules have been omitted for clarity.

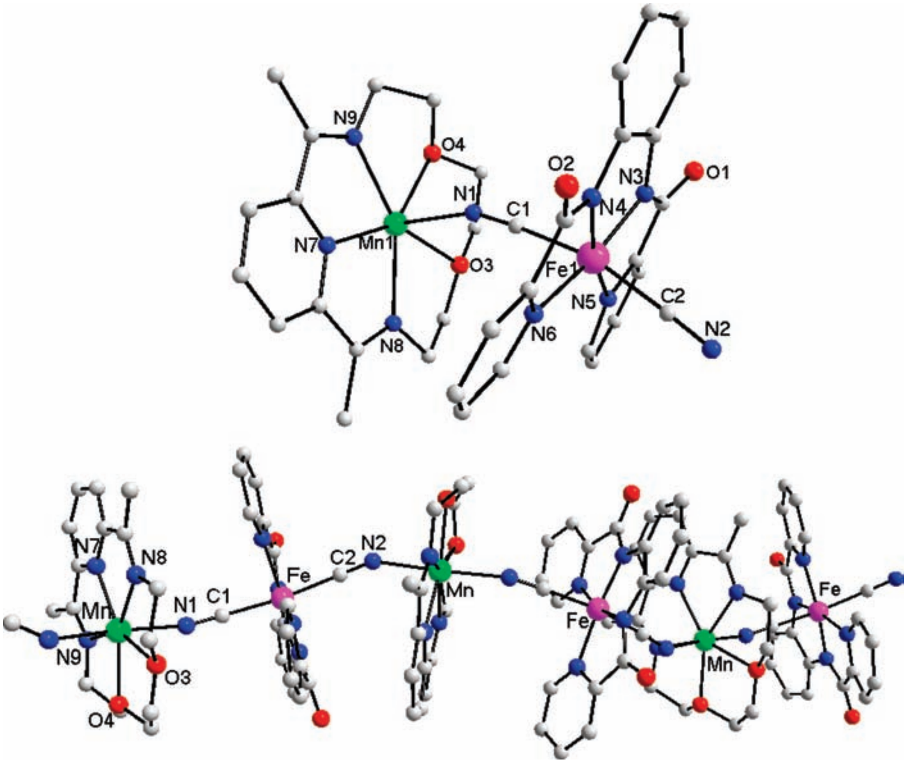


Figure 3. Asymmetry cationic unit and 1D cationic chain structure of complex **3**. All the hydrogen atoms, free ClO_4^-, and solvent water molecules have been omitted for clarity.

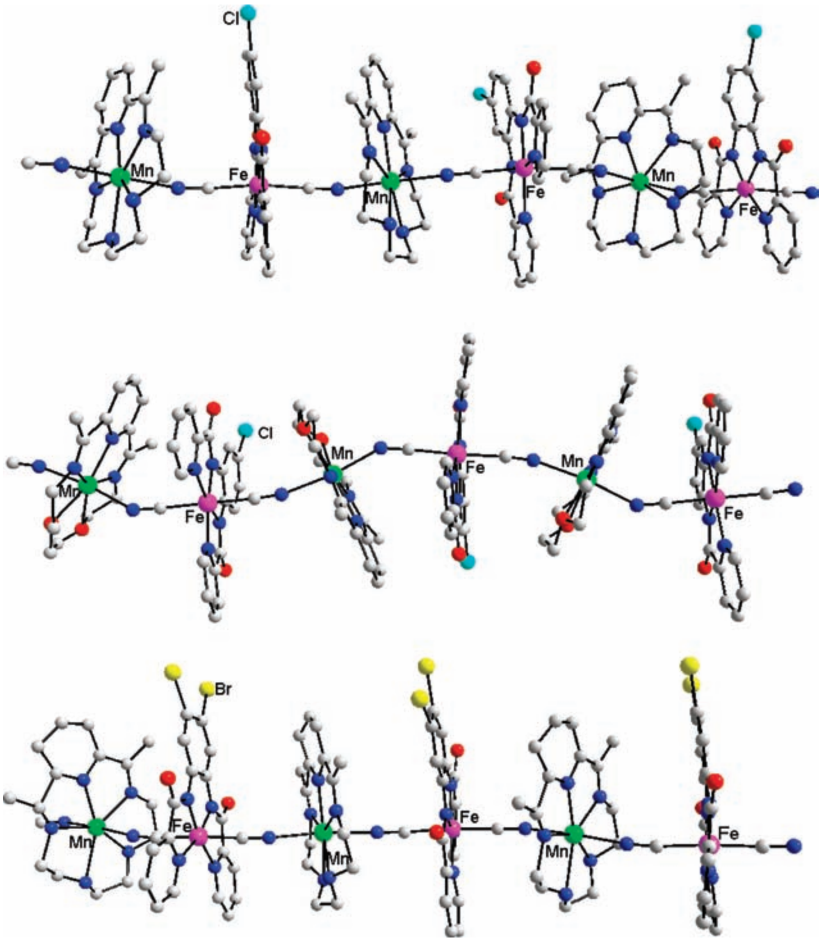


Figure 4. One-dimensional cationic structures of complex **4** (top), **5** (middle), and **6** (bottom). All the hydrogen atoms, free ClO_4^- anions, and solvent water molecules have been omitted for clarity.

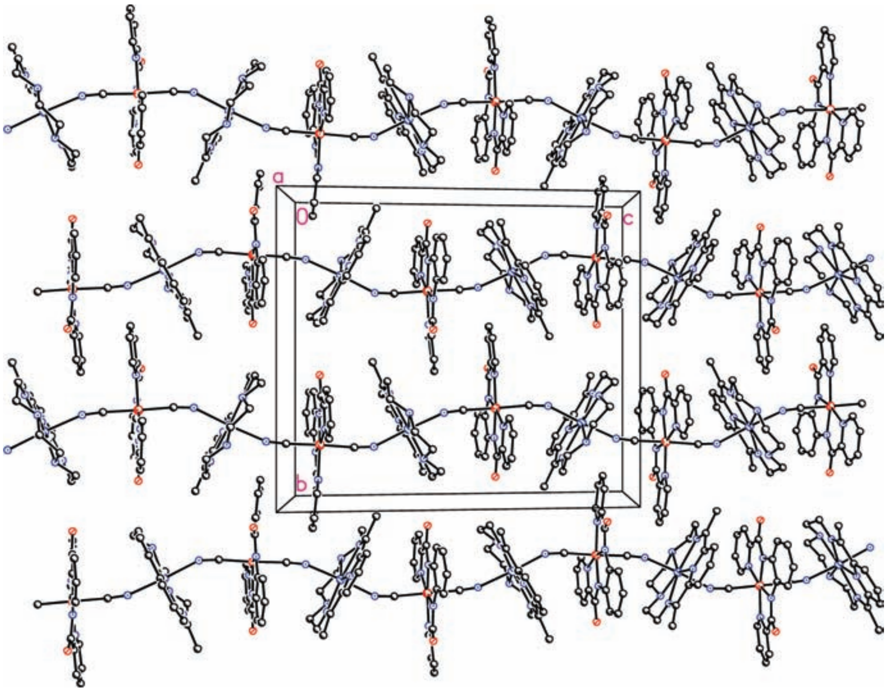
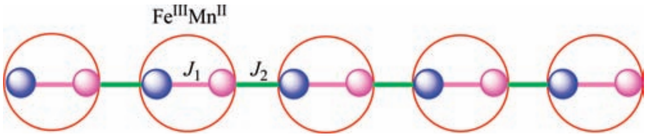


Figure 5. Representative cell packing diagram for complexes **2**, **4**, and **6** along *a* axis. The balanced anion, water, and all the hydrogen atoms have been omitted for clarity.

Scheme 2



and attains their highest value of 3.87 emu K mol^{-1} for **3** and 4.76 emu K mol^{-1} for **5** with the temperature decreasing to 2 K. The magnetic susceptibilities for these five complexes conform well to the Curie−Weiss law in the range of 2−300 K and give the negative Weiss constant and Curie constant listed in Table 3. These data, in combination with the changing tendency of $\chi_m T-T$, lead to a primary conclusion that the magnetic coupling between Fe(III) and Mn(II) bridged by the cyanide group in all the five complexes is antiferromagnetic.

To analyze the magnetic data of these five cyanide-bridged 1D heterometallic $Fe^{III}-Mn^{II}$ single chain complexes, an approximate approach similar to that previously used for heterometallic 1D and quasi-2D complexes was employed.[18c,29,30] According to the crystal data, the Fe(III)-CN-Mn(II) linkage is unequal. Therefore, the 1D single chain can be treated as alternating uniform $Fe^{III}Mn^{II}$ dimers with different intradimeric and intrachain (also interdimer) exchange constant (J_1 vs. J_2), and the susceptibilities over the temperature range of 2−300 K for all the five complexes could be simulated by using this model (Scheme 2). The best-fit parameters obtained have been given in Table 3.

$$\chi_d = \frac{Ng^2\beta^2}{kT}\frac{28+10\exp(-6J_1/kT)}{7+5\exp(-6J_1/kT)} \tag{1}$$

$$\chi_d = \frac{Ng^2\beta^2}{3kT}S_d(S_d+1) \tag{2}$$

$$\chi_{chain} = \frac{Ng^2\beta^2}{3kT}\frac{1+u}{1-u}\times S_d(S_d+1) \tag{3}$$

$$\chi_m = \frac{\chi_{chain}}{1-\chi_{chain}(2zJ'/Ng^2\beta^2)} \tag{4}$$

where $u = \coth(J_2S_d(S_d+1)/kT) - kT/J_2S_d(S_d+1)$.

Furthermore, the magnetic susceptibilities for these 1D complexes have also been simulated by using MAGPACK program[31] with the experimental $\chi_m T$ value of 2−300 K. According to the method which has been employed to simulate the magnetic susceptibilities of 1D chain compounds with alternating spins 1/2 and 2 successfully,[31b] the five 1D chain compounds can be considered as isotropic Heisenberg chains containing alternating spins 1/2 and 5/2 with two antiferromagnetic exchange interactions J_1 and J_2. In this case, the magnetic susceptibilities of the infinite single chain can be simulated and calculated rationally and satisfactorily based on a closed ring cluster model consisting of five pairs of 1/2−5/2 with two alternating antiferromagnetic exchange interactions J_1 and J_2, Scheme 3.

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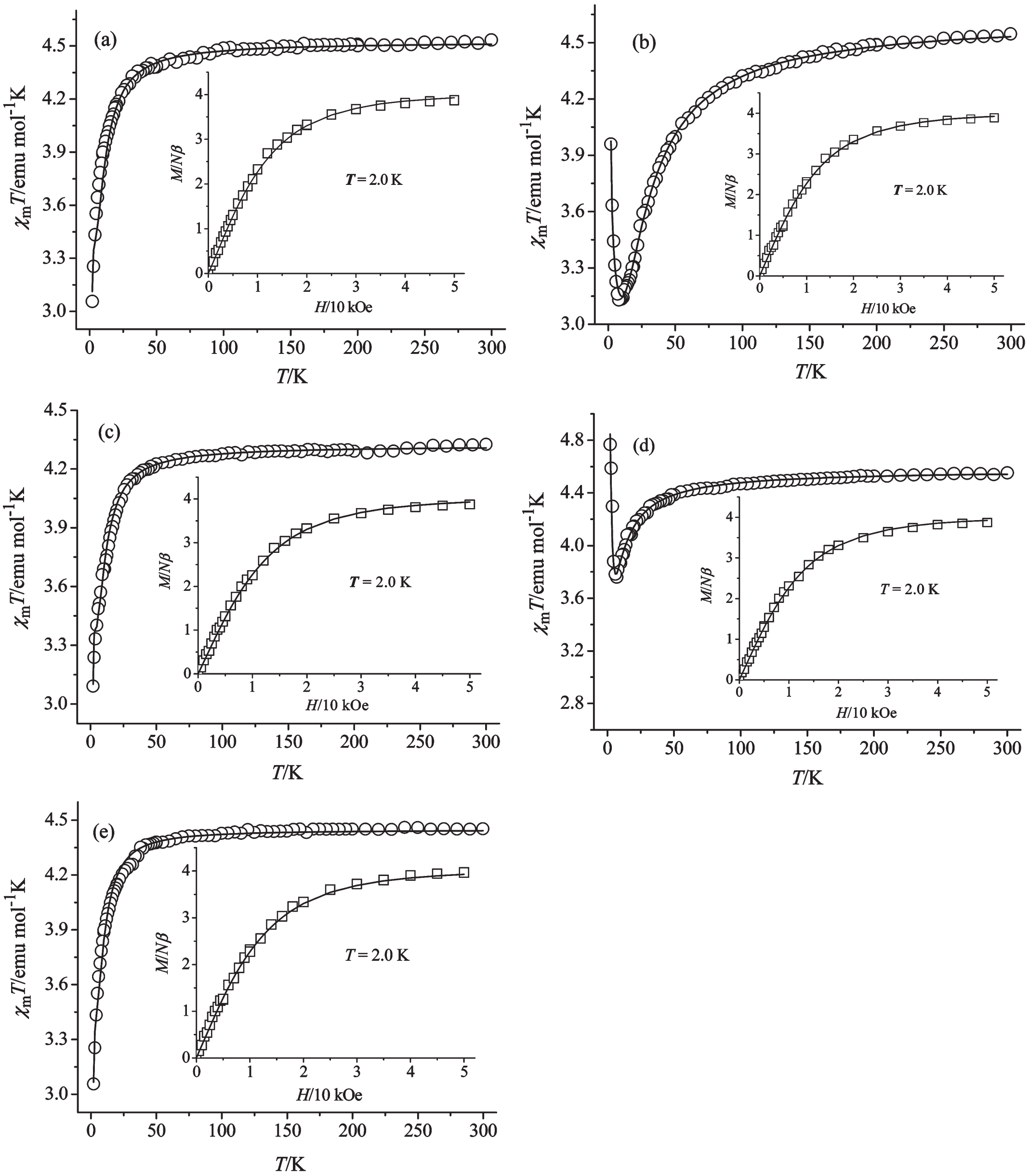

Figure 6. Temperature dependence of χ_mT of complexes **2** (a), **3** (b), **4** (c), **5** (d), and **6** (e) (the solid line represents the best fit based on the parameters discussed in the text). Inset: Field dependence of magnetization at 2 K (the dotted line is the Brillouin curve for coupled Fe(III) and Mn(II) ions with g = 2.0).

Table 3. Magnetic Parameters of Complexes **2**−**6**

	θ (K)	C (emu K mol^{-1})	model fit					MAGPACK program fit			
			J_1 (cm^{-1})	J_2 (cm^{-1})	zJ' (cm^{-1})	g	R ($\times10^{-5}$)	J_1 (cm^{-1})	J_2 (cm^{-1})	g	R ($\times10^{-5}$)
2	−1.73	4.55	−1.16(2)	−0.10(3)	−0.15(6)	1.98(2)	2.09	−1.32(5)	−0.14(1)	1.99(7)	3.04
3	−6.14	4.62	−3.10(1)	−0.25(1)	−0.32(3)	1.97(8)	1.49	−3.43(2)	−0.32(3)	1.98(2)	1.78
4	−1.61	4.31	−1.10(1)	−0.14(8)	−0.17(3)	1.99(6)	1.72	−1.31(5)	−0.15(5)	1.95(1)	2.12
5	−1.89	4.56	−1.99(6)	−0.57(1)	−0.28(4)	1.98(7)	2.12	−1.79(2)	−0.62(4)	2.03(1)	2.34
6	−1.41	4.48	−1.23(1)	−0.13(5)	−0.19(2)	1.99(2)	1.62	−1.31(1)	−0.14(7)	1.98(9)	1.73

The best-fit parameters obtained from this method are tabulated in Table 3, and the fitting diagrams are given in Supporting Information, Figure S2. These values are basically consistent with those obtained employing the model method. It is worth noting that since the contributions from intercomplex interactions (zJ') were neglected during the simulation process, the J values obtained here might be slightly overestimated. However, as can be found, the J values for these complexes are comparable to each other and also to those found for other cyanide-bridged Fe^{III}−Mn^{II} clusters.[18a,18b,32] The slight difference among different complexes of **2**−**6** is attributed to the slight difference in their molecular structure.

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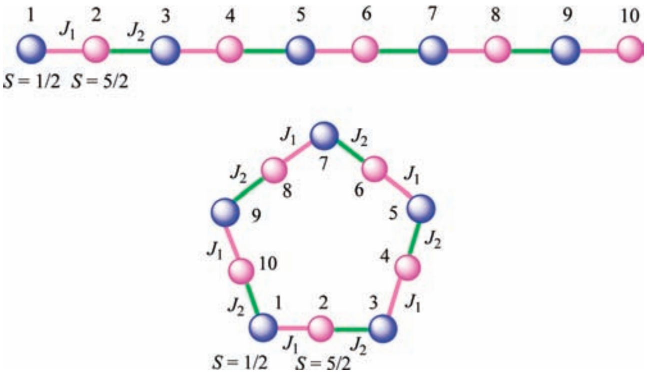
Scheme 3



The field-dependent magnetizations measured up to 50 kOe at 2 K for complexes **2**−**6** are shown in the inset of Figure 6. All the curves have a similar changeable tendency. The magnetization increases with a relatively fast speed with increasing field until 15 kOe, then increases smoothly up to about 3.9 Nβ until 50 kOe. This data is very close to the saturated value of 4.0 Nβ but obviously lower than the value of uncoupled Mn(II) and low spin Fe(III) based on $g = 2.0$, confirming again the overall antiferromagnetic coupling interaction between Fe(III) and Mn(II) ions bridged by cyanide group.

All the five cyanide-bridged 1D $Fe^{III}-Mn^{II}$ complexes exhibit overall antiferromagnetic coupling between Fe (III) and Mn(II) ions through the cyanide bridge. As usual, the presence of a net overlap of the magnetic orbitals through the π (t_{2g}-t_{2g}) pathways [$t_{2g}^3e_g^2$ and $t_{2g}^5e_g^0$ configurations for Mn(II) and Fe(III), respectively] is considered to overwhelm the ferromagnetic term of the $\sigma-\pi$ (t_{2g}-e_g) orthogonal coupling for these compounds. The variation of J value in these complexes can be attributed to the structural difference such as coordination surrounding around Mn(II) ion, the bond bending of Mn−N≡C−Fe linkage, and Mn−N$_{\text{cyanide}}$ bond distance. The present work further confirms the fact that most cyanide-bridged $Fe^{III}-Mn^{II}$ complexes reported previously exhibit antiferromagnetic interaction with few exceptions.[18a,26a,33]

Conclusion

In summary, a new series of heterobimetallic cyanide-bridged $Fe^{III}-Mn^{II}$ 1D single chain complexes have been rationally designed and successfully synthesized using three dicyanide-containing compounds and two seven-coordinated macrocycllic Mn(II) compounds as building blocks. Investigation over their magnetic properties reveals an overall antiferromagnetic interaction between Fe(III) and Mn(II) ions bridged by the cyanide group. The present work will be helpful in providing valuable information for the rational design and synthesis of low-dimensional cyanide-bridged magnetic complexes. Synthesis and magnetic investigation of other series of cyanide-bridged heterometallic 1D complexes with interesting magnetic properties, in particular, of single chain magnet nature using appropriate spin carriers as building blocks, are under way.

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Supporting Information Available: Crystallographic data in CIF format. The representative cell packing diagrams for complexes **3** and **5**. Temperature dependences of $\chi_m T$ of complexes **2**−**6** and their fitting diagram by using the MAGPACK program. This material is available free of charge via the Internet at http://pubs.acs.org.

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