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ARTICLE TYPE

Synthesis, Crystal Structures and Magnetic Properties of *mer*-Cyanideiron(III)-Based 1D Heterobimetallic Cyanide-Bridged Chiral Coordination Polymers

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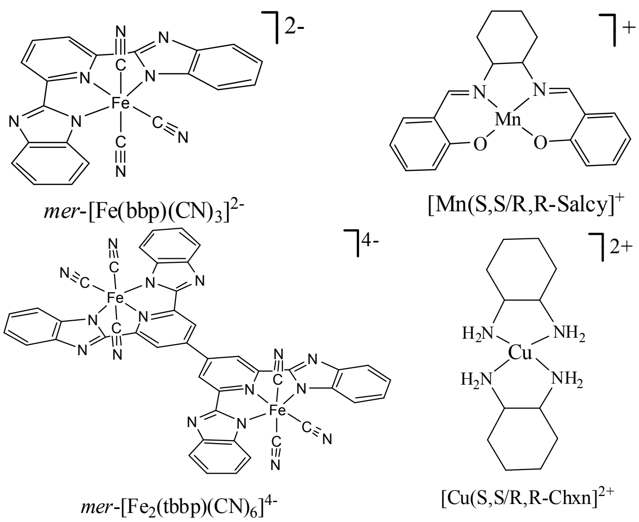
Two pairs of cyanide-bridged Fe(III)-Mn(III)/Cu(II) chiral enantiomer coordination polymers {[Mn(S,S/R,R-Salcy)$(CH_3OH)_2$]{[Mn(S,S/R,R-Salcy)][Fe(bbp)$(CN)_3$]}}$_{2n}$ (**1**,**2**) (bbp = bis(2-benzimidazolyl)pyridine dianion) and {[Cu(S,S/R,R-Chxn)$_2$]$_2$[Fe_2(tbbp)$(CN)_6$]}$_n$ (**3**,**4**) (tbbp = tetra(3-benzimidazolyl)-4,4'-bipyridine tetraanion) have been successfully prepared by employing *mer*-tricyanometallate $[PPh_4]_2$[Fe(bbp)$(CN)_3$] or the newly bimetallic *mer*-cyanideiron(III) precursor K_4[Fe_2(tbbp)$(CN)_6$] as building block and with chiral manganese(III)/copper(II) compounds as assemble segments. The four complexes have been characterized by elemental analysis, IR spectroscopy, circular dichroism (CD) and magnetic circular dichroism (MCD) spectrum. Single X-ray diffraction reveals complexes **1** and **2** possess single anionic chain structure consisting of the asymmetric chiral {[Mn(S,S/R,R-Salcy)][Fe(bbp)$(CN)_3$]}$_2^{2-}$ unit with free [Mn(S,S/R,R-Salcy)]$^+$ as balanced cations. The cyanide-bridged Fe(III)-Cu(II) complexes **3** and **4** can be structurally characterized as neutral ladder-like double chain composed by the alternating cyanide-bridged Fe-Cu units. Investigation over magnetic susceptibilities reveals the antiferromagnetic coupling between the cyanide-bridged Fe(III) and Mn(III)/Cu(II) ions for complexes **1**-**4**. These results have been further confirmed by theoretical simulation through numerical matrix diagonalization techniques by using a Fortran program or an uniform chain model, leading to the coupling constants J= -7.36 cm^{-1}, D =-1.52 cm^{-1} (**1**) and J = -4.35 cm^{-1} (**3**), respectively.

Introduction

Due to their fundamental interest and potential applications in magnetic devices,[1-4] molecule-based magnetic materials have been explored intensively in the past three decades. One of the outstanding merits for this type of magnetic materials is that specific magnetic traits in the molecular solids can be inserted intentionally by employing the emergent intrinsic properties of compositional metal centers and ligands with various functionalities,[5,6] which can provide plenty of intriguing characteristics in molecular assemblies such as anisotropy related magnetism, chirality, magnetization-induced second harmonic generation, photomagnetism, and so on.[7,8] Among which, for the well known reasons, cyanide-bridged molecular magnetic materials have been actively studied because of their growing interest in the field of molecular magnetism covering high-TC magnets,[9-10] photomagnets,[11-13] spin-crossover material,[14-16] chiral magnets[17-21], single-molecule magnets (SMMs),[22-24] and single chain magnets (SCMs).[25-27]

The rational design of cyanide-bridged magnetic materials can be achieved following a building-block approach with the premeditated association of various complexes and blocked cyanidometallates $[M(L)_x(CN)_y]^{z-}$ (L = *mono*- or *multi*-dentate organic ligand). Thus far, a family of original magnetic complexes with controlled structures and properties have been prepared by selection of appropriate cyano building blocks exhibiting targeted chemical (number of cyanido groups, steric hindrance of the ligand, etc.) and physical properties (local anisotropy, spin state, etc.)[28-29]. Precursors including Fe(III) ion with magnetic anisotropy caped by different organic ligand(s) have essentially attracted attention in pursuit of designing magnetically anisotropic assemblies with low-dimensional structures. As for *tri*-cyanideiron(III) molecular building bricks $[Fe(L)(CN)_3]^-$, there are two isomeric forms with *facial* and *meridional* dispositions defined by the relative positioning of the three cyanide ligands around the Fe atom. A great number of molecular clusters and 1D chains have been reported based on *fac*-Fe(A)$(CN)_3]^-$[30-36] (A = hydrotris(3,5-dimethylpyrazol-1-yl)borate (Tp*), tetra(pyrazol-1-yl)borate (pzTp), and 1,3,5-triaminocyclohexane (tach)) or *mer*- Fe(B)$(CN)_3]^-$ (B = bis(2-pyridylcarbonyl)amidate anion (bpca), 8-(pyridine-2-carboxamido)quinoline anion (pcq), 8-(pyrazine-2-carboxamido)quinoline anion (pzcq), 8-(5-methylpyrazine-2-carboxamido)quinoline anion (mpzcq), and 8-(2-quinolinecarboxamido)quinoline anion (qcq), *N*-(quinolin-8-yl)isoquinoline-1-carboxamide ion (iqc)[37-40], in which some often accompany interesting magnetic properties of SMM, SCM, chirality, ferroelectricity, and photomagnetism.[41-49]. On the other hand, the elucidation of the magnetic exchange coupling mechanism provides essential information on the magnetic phenomena of molecular systems. As can be found from the examples assembled from tricyanideiron(III) precursors and Mn(III) quadridentate Schiff-bases compounds, for the latter which always showed sizable anisotropic characteristics due to the large spin (S = 2) and the intrinsic Jahn-Teller elongations in axial directions, the magnetic properties of *fac*-Fe tricyanide-linked compounds are mostly ferromagnetic, while antiferromagnetic interactions are almost exclusively visible in *mer*-Fe tricyanide-bridged complexes so far[39d,40]. Aiming to synthesize new bifunctional materials, and also for the purpose of further gaining some insight into a fundamental magneto structural relationship of the Fe(III)–C≡N–Mn(III) unit, two *mer*-Fe building blocks containing one or two low spin Fe(III) ion(s) (Scheme 1), which own the different steric effect and charge numbers from the previously used *mer*-tricyanideiron(III) precursors, and four chiral manganese(III)/copper(II) compounds have been employed to assemble cyanide-bridged system, resulting in two pairs of cyanide-bridged heterometallic enantiomer complexes $\{[Mn(S,S\text{-}Salcy)(CH_3OH)_2]\{[Mn(S,S\text{-}Salcy)][Fe(bbp)(CN)_3]\}\}_{2n}\cdot nCH_3CN\cdot 6nCH_3OH\cdot 2nH_2O$ (**1**), $\{[Mn(R,R\text{-}Salcy)(CH_3OH)_2]\{[Mn(S,S\text{-}Salcy)][Fe(bbp)(CN)_3]\}\}_{2n}\cdot nCH_3CN\cdot 6nCH_3OH\cdot 2nH_2O$ (**2**) (bbp = bis(2-benzimidazolyl)pyridine dianion), $\{[Cu(S,S\text{-}Chxn)_2]_2[Fe_2(tbbp)(CN)_6]\}_n\cdot 2nDMF\cdot 2nCH_3OH\cdot 3nH_2O$ (**3**) and $\{[Cu(R,R\text{-}Chxn)_2]_2[Fe_2(tbbp)(CN)_6]\}_n\cdot 2nDMF\cdot 2nCH_3OH\cdot 7nH_2O$ (**4**) (tbbp = tetra(3-benzimidazolyl)-4,4'-bipyridine tetraanion). (Scheme 1) The synthesis, crystal structures and magnetic properties of the four new complexes will be described in this paper. It should be noted that, to our best of the knowledge, it is the first time that cyanide precursor containing bimetallic paramagnetic centers is used to prepare cyanide-bridged magnetic complexes.



Scheme 1. The starting materials used to prepare the complexes **1**-**4**.

Experimental Section

Elemental analyses of carbon, hydrogen, and nitrogen were carried out with an Elementary Vario El (Supporting information). 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. $Mn((S,S/R,R)\text{-}Salcy)(H_2O)_2]ClO_4$ were prepared as described for other manganese Schiff-base compounds in literature.[50] The H_2bbp ligand has been prepared previously.[51] The method for the synthesis of $[PPh_4]_2[Fe(bbp)(CN)_3]$ was similar to that for $[NEt_4]_2[Fe(bbp)(CN)_3]$.[52]

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.

Synthesis of the ligand H_4tbbp: Phosphoric acid (20 mL) containing H_4BPTC (1,1'-biphenyl-2,2',6,6'-tetracarboxylic acid)[53] (1.66 g, 5 mmol) and *o*-phenylenediamine (2.14 g, 20 mmol) was heated to 220-230^o for 4 hours under N_2 atmosphere. The deep colored mixture was poured into 500 ml of vigorously stirred ice-water mixture. The deep blue precipitate was filtered out after cooling to room temperature, then suspended in 10% aqueous sodium carbonate solution under the stirring condition. The resulting solid was collected by filtration and recrystallized from methanol and water (1:1, v:v) to give offwhite crystalline solid with the yield about 50%. Anal. Calcd for $C_{38}H_{24}N_{10}$: C, 73.54; H, 3.90; N, 22.57. Found: C, 72.91; H, 4.79; N, 22.75.

Synthesis of $K_4[Fe_2(tbbp)(CN)_6]$: H_4TBBP (0.62g, 1 mmol) was added to a methanol solution (30 mL) of $FeCl_3$ (0.33g, 2 mmol) little by little, and the obtained mixture was refluxed for two hours before an aqueous solution of KCN (0.65g, 10 mmol) was added. After an additional 6 h reflux, the solution became deep blue, then the mixture was evaporated to dryness under the reduced pressure, and then the dark-blue residue was dissolved in DMF (15 mL) with stirring. After the unreacted KCN was filtered out, the DMF solution was condensed to about one-third on rotary evaporator, and excess ether was added to precipitate the blue crystalline solid. Yield: 0.6g, 58%. Anal. Calcd for $C_{44}H_{20}Fe_2K_4N_{16}$: C, 50.77; H, 2.94; N, 21.53. Found: C, 50.95; H, 3.19; N, 20.96. Main IR bands (cm^{-1}): 2115 (s, νC≡N).

Synthesis of complexes 1 and 2. To a solution of $[PPh_4]_2[Fe(bbp)(CN)_3]$ (112 mg, 0.10 mmol) in methanol (10 mL), $[Mn(S,S\text{-}Salcy)(H_2O)_2]ClO_4$ or $[Mn(R,R\text{-}Salcy)(H_2O)_2]ClO_4$ (102.2 mg, 0.20 mmol) dissolved in methanol/acetonitrile (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 one week, dark-brown block crystals were collected by filtration.

Complex **1**: Yield: 78.1 mg, 56.1%. Anal. Calcd for $C_{136}H_{149}Fe_2Mn_4N_{25}O_{20}$: C, 58.64; H, 5.39; N, 12.57. Found: C, 58.45; H, 5.19; N, 12.76. Main IR bands (cm^{-1}): 2150 (s, νC≡N), 2117 (s, νC≡N), 1620 (vs, νC=N).

Complex **2**: Yield: 74.5 mg, 53.5%. Anal. Calcd for $C_{136}H_{149}Fe_2Mn_4N_{25}O_{20}$: C, 58.64; H, 5.39; N, 12.57. Found: C, 58.41; H, 5.13; N, 12.69. Main IR bands (cm^{-1}): 2148 (s, νC≡N), 2118 (s, νC≡N), 1615 (vs, νC=N).

Synthesis of complexes 3 and 4. $K_4[Fe_2(tbbp)(CN)_6]$ (110 mg, 0.10 mmol) dissolved in methanol (10 mL) was added to a acetonitrile solution (10 mL) containing $[Cu(ClO_4)_2]\cdot 6H_2O$ (73.0 mg, 0.2 mmol) and R,R/S,S-1,2-diaminocyclohexane (45.6 mg, 0.4 mmol). Then, DMF was added dropwise with stirring until the precipitation dissolved completely. The dark-green crystals suitable for X-ray diffraction were grown out from the filtration after slow evaporation of the solvent for about one month.

Complex **3**: Yield: 98.8 mg, 57.1%. Anal. Calcd. for $C_{76}H_{104}Cu_2Fe_2N_{26}O_7$: C, 52.68; H, 6.05; N, 21.02. Found: C, 52.34; H, 5.74; N, 21.46. Main IR bands (cm^{-1}): 2155, 2120 (s, νC≡N), 1630 (vs, νC=N).

Complex **4**: Yield: 102 mg, 56.54%. Anal. Calcd. for $C_{76}H_{112}Cu_2Fe_2N_{26}O_{11}$: C, 50.58; H, 6.26; N, 20.18. Found: C, 50.22; H, 6.11; N, 20.48. Main IR bands (cm^{-1}): 2157, 2120 (s, νC≡N), 1632 (vs, νC=N).

X-ray data collection and structure refinement. Data were collected on a Oxford Diffraction Gemini E diffractometer with Mo *Kα* radiation (λ = 0.71073 Å) at 293 K. Final unit cell parameters were derived by global refinements of reflections obtained from integration of all the frame data. The collected frames were integrated by using the preliminary cell-orientation matrix. CrysAlisPro Agilent Technologies software was used for collecting frames of data, indexing reflections, and determination of lattice constants; CrysAlisPro Agilent Technologies for integration of intensity of reflections and scaling, SCALE3 ABSPACK for absorption correction. The structures were solved by the direct method (*SHELXS-97*) and refined by full-matrix least-squares (*SHELXL-97*) on F^2. Anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. Hydrogen atoms were added geometrically and refined using a riding model. Selected bond distances and bond angles for complexes **1-4** with their estimated standard deviation are listed in Table 1. CCDC 995710, 995711, 995714 and 995715 for complexes **1-4** 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.

Table 1. Crystallographic data for complexes **1-4**.

	1	2	3	4
Chemical formula	$C_{136}H_{149}Fe_2Mn_4N_{25}O_{20}$	$C_{136}H_{149}Fe_2Mn_4N_{25}O_{20}$	$C_{76}H_{104}Cu_2Fe_2N_{26}O_7$	$C_{76}H_{112}Cu_2Fe_2N_{26}O_{11}$
Fw	2785.26	2785.26	1732.63	1804.70
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	P2(1)	P2(1)	P1	P1
a/Å	19.5092(4)	19.5297(5)	10.2833(16)	10.2968(6)
b/Å	14.9489(2)	14.9492(4)	13.8961(18)	13.7993(8)
c/Å	22.5356(4)	22.5824(5)	18.0725(12)	17.7819(9)
α/deg	90	90	79.813(8)	80.207(4)
β/deg	98.240(2)	98.188(2)	85.233(8)	84.697(4)
γ/deg	90	90	68.301(13)	69.378(5)
V/Å^3	6504.5(2)	6525.8(3)	2361.3(5)	2328.8(2)
Z	2	2	1	1
F(000)	2904	2904	908	948
GOF	1.025	1.015	1.051	1.025
$R_1[I > 2\sigma(I)]$	0.0399	0.0614	0.0746	0.0658
wR_2(all data)	0.1005	0.1459	0.2477	0.1804

Results and discussions

Synthesis and general characterization

Low-dimensional cyanide-bridged complexes have attracted more and more attention for the purpose of clearly elucidating magneto-structural correlation 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, number and nature of charge of cyanide-containing building block, and steric effect of reactants must be taken into account. Considering that the different steric effect and the number of the charges of *mer*-$[Fe(bbp)(CN)_3]^{2-}$ from the other previously reported *mer*-tricyandieiron building blocks,[37-40] we investigated the reactions of *mer*-$[Fe(bbp)(CN)_3]^{2-}$ with chiral Schiff-base manganese compounds, and obtained two cyanide-bridged enantiomers structurally characterized as anionic single chain. By introducing bipyridine skeleton into the cyanide-precursor, a new *mer*-cyano building block containing two paramagnetic low spin iron(III) ions was synthesized for the first time, and two cyanide-bridged Fe(III)-Cu(II) one-dimensional ladder-like double chain enantiomers have been prepared based-on *mer*-$[Fe_2(tbbp)(CN)_6]^{4-}$ and chiral amine-based copper compounds.

The four cyanide-bridged complexes, as well as $K_4[Fe_2(tbbp)(CN)_6]$, have been characterized by IR spectroscopy. In the IR spectra of $K_4[Fe_2(tbbp)(CN)_6]$, the absorption locating at about 2115 cm^{-1} was assigned to the terminal cyanide group. For complexes **1-4**, two sharp peaks due to the cyanide-stretching vibration were observed in the range of 2125-2160 cm^{-1}, respectively, indicating the presence of bridging and nonbridging cyanide ligands in these complexes. To confirm the optical activity and enantiomeric nature, the circular dichroism (CD) spectrum were measured in KBr pellets for complexes **1-4**. The CD spectrum of **1**,**2** and **3**,**4** exhibit positive and negative Cotton effect at the same wavelengths (Figure 1). The Magnetic circular dichroism (MCD) spectra for complexes **1** and **3** were recorded on a JASCO-815 spectrodichrometer equipped with a JASCO electromagnet, which produces magnetic fields of 1.60 T with both parallel and antiparallel fields. The magnitudes ($[\theta]_M$) were expressed in terms of molar ellipticity per tesla (deg $dm^3mol^{-1}cm^{-1}T^{-1}$) (Figure S1-S2, ESI).

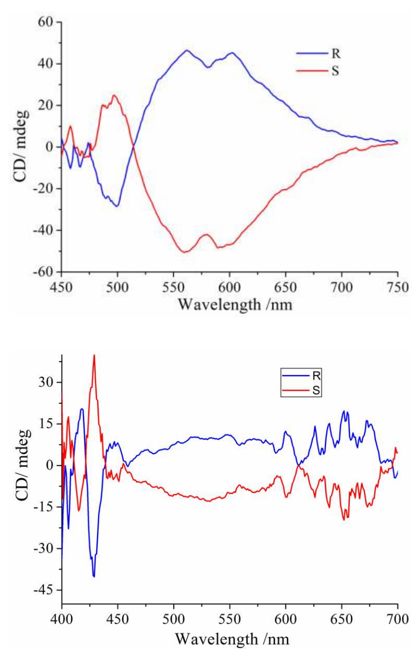


Figure 1. CD spectra of **1**(*S* isomer, red), **2**(*R* isomer, blue) (top) and **3**, **4** (bottom) in KBr pellets.

Crystal Structure of Complexes 1-4.

Some important structural parameters for complexes **1**-**4** are collected in Tables S1 and S2 (ESI). Complexes **1** and **2** crystallized in the chiral space group P2(1) are enantiomers, therefore complex **1** is as representative for the detailed structure description. The anionic asymmetry unit, the one-dimensional anionic structure, and the cell packing diagram for complex **1** are depicted in Figures 1-3, respectively. As can be found, this compound possesses perfect one dimensional anionic infinite structure comprising of repeating $\{[Mn(S,S/R,R\text{-}Salcy)][Fe(bbp)(CN)_3]\}_2^{2-}$ unit with the negative charges balanced by $[Mn(S,S/R,R\text{-}Salcy)]^+$ cations. Each *mer*-$[Fe(bbp)(CN)_3]^{2-}$ unit, acting as a bidentate ligand through its two cyanide groups in a *trans* position, connects the Mn(III) ions of two independent $[Mn(S,S/R,R\text{-}Salcy)]^+$ units. The Fe atom is coordinated by three N atoms of cyanide precursor located in the equatorial plane and three C atoms of cyanide groups in *mer*-position, forming a slightly distorted octahedral geometry, which can be testified by the parameters around the Fe atom listed in Table S1.

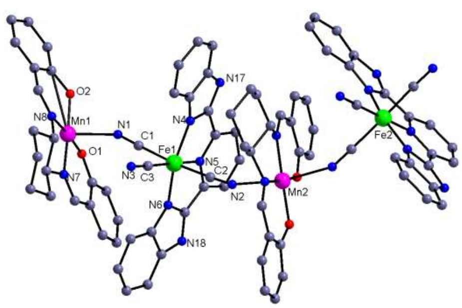


Figure 1. The asymmetry anionic unit of complex 1. All the hydrogen atoms, the balanced cations and the solvent molecules have been omitted for clarity.

Both of the intrachain and the isolated Mn(III) ions are six-coordinated, also forming a slightly distorted octahedron coordination geometry, in which the four equatorial positions are occupied by a N_2O_2 unit coming from the chiral Schiff-base ligand. For the two axial ones, they are coordinated by two N atoms of cyanide groups for the intrachain Mn(III) ion and two O atoms from the solvent methanol molecules for the free one, respectively. The $Mn\text{-}N_{cyanide}$ bond lengths in complex **1** are 2.319(3) and 2.263(2) Å (with Mn1 as example), respectively, obviously longer than $Mn\text{-}N_{Schiff\text{-}base}$ and $Mn\text{-}O_{Schiff\text{-}base}$ bond lengths with the average values of 1.999 and 1.879 Å, which gives further information about the elongation octahedron surrounding the Mn(III) ion, typically accounting for the well known Jahn-Teller effect. As tabulated in Table 2, the bond angle of $N_{cyanide}\text{-}Mn1\text{-}N_{cyanide}$ is 169.44(11)^o, indicating the almost linear configuration of these three atoms. However, the Mn-N≡C bond angles are somewhat bent with the values of 151.5(3) and 157.1(3) ^{o}, respectively. The torsion angle (ϕ) of Mn-N≡C-Fe, which is defined as the rotation of the *x* and *z* axes for Mn(III) compared with the *xz* plane for Fe(III), is 7.59^o in complex **1**. The intramolecular $Fe^{III}\text{-}Mn^{III}$ separation through bridging cyanide is about 5.15 Å, while the shortest intermolecular metal-metal distance 7.272 Å is obviously longer than this value.

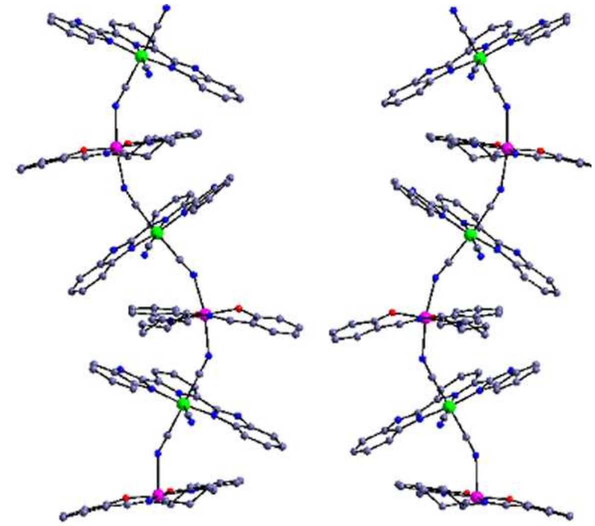


Figure 2. Perspective view along *b* axis of the one-dimensional infinite chains of **1** (S,S isomer, left) and **2** (R,R isomer, right), respectively.

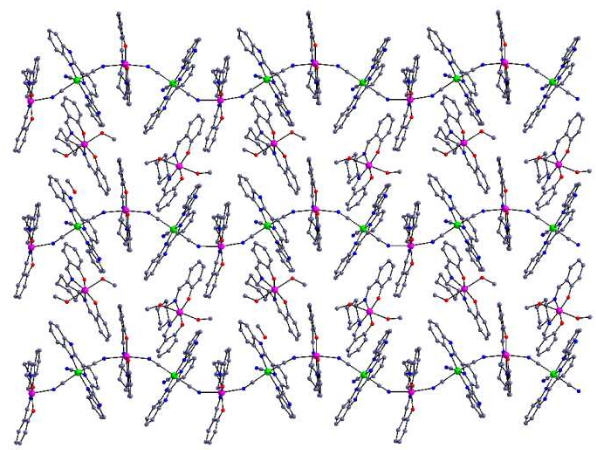


Figure 3. The cell packing diagram along *c* axis of complex **1**. All the H atoms have been omitted for clarity.

For complexes **3** and **4**, the neutral molecular structure containing Fe_2Cu_2 core and the ladder-like double chain is given in Figure 4. The perspective view of the enantiomer structure of these two complexes and their representative cell packing diagram are shown in Figures S3 and S4 (ESI), respectively. Complexes **3** and **4** crystallized in triclinic space group P1 are also one pair of enantiomers, which can be structurally characterized as bipyridine and cyanide-bridged ladder-like double chain. As listed in Table S2, the coordination geometry of the Fe(III) is a slightly distorted octahedron with the parameters similar to those in complexes **1** and **2**. The coordination sphere for the Cu(II) atom in these two complexes is also octahedral, in which the equatorial positions are occupied by four N atoms of two 1,2-diaminocyclohexane ligands, while the two axial sites are occupied by the N atoms of the bridging cyanide groups. The average distances between the Cu atom(with Cu1 as representative) and the N atoms of 1,2-diaminocyclohexane are 1.97 Å in complex **3**, while the average $Cu\text{-}N_{cyanide}$ bond length is 2.537 Å, which is markedly longer than the above bond lengths, indicating the obvious distortion of the octahedron along the $N_{cyanide}$-Cu-$N_{cyanide}$ axis. The angles of the C≡N-Cu moieties in complex **3** are 140.8(9) and 131.7(10)°, respectively, showing clearly that these groups seriously eviate from a linear configuration. The two torsion Fe-C≡N-Cu angles in complex **3** are 10.56 and 9.96°, respectively. The intramolecular Fe^{III}-Cu^{II} separations through the bridging cyanide groups is about 5.12 Å for complex **3**, while the shortest intermolecular M…M distance is 10.074 Å.

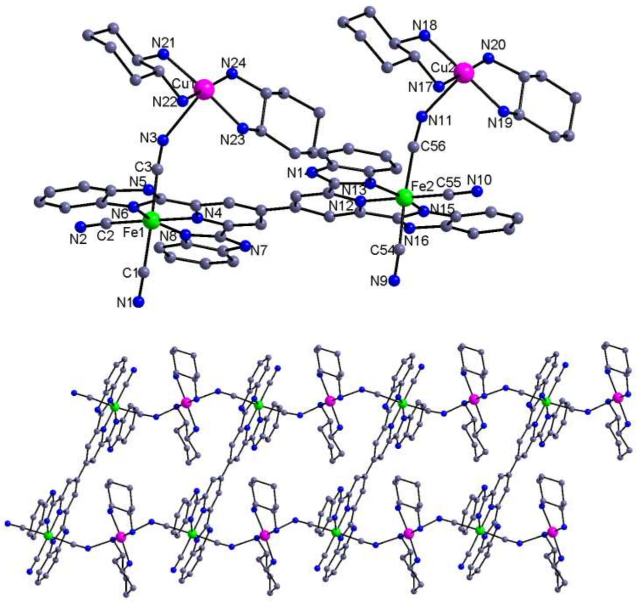


Figure 4. The Fe_2Cu_2 unit and the ladder-like double chain structure of complexes **3** and **4** along *c* axis. All the solvent H atoms and the solvent molecules have been omitted for clarity.

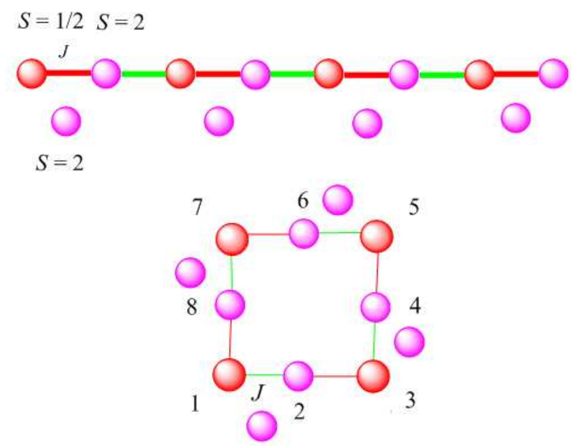
The Magnetic properties of complexes 1 and 2.

The temperature dependence of magnetic susceptibility for these two complexes was measured in the range of 2-300 K under the external magnetic field of 2000 Oe (Figure 5 and Figure S5, ESI). The $\chi_m T$ value per $Fe^{III}Mn^{III}_2$ unit at room temperature is 6.20 emu K mol^{-1} (with complex **1** as representative), which is slightly lower than the spin only value of 6.375 emu K mol^{-1} for two uncoupled Mn(III) (S = 2) ion and a low spin Fe(III) (S = 1/2) ion based on g = 2.00. With decreasing the temperature, the $\chi_m T$ value decreases slowly and attains the value of 5.78 emu K mol^{-1} at about 50 K, respectively. After this, the $\chi_m T$ value starts to decrease steeply and reaches its lowest value 4.39 emu K mol^{-1} at 2 K. The magnetic susceptibility for complex **1** conform well to Curie-Weiss law in the range of 10-300 K and give the negative Weiss constant θ = -2.46 K and Curie constant C = 6.25 emu K mol^{-1}. 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(III) bridged by cyanide group is antiferromagnetic.

To analyze the magnetic data of this one-dimensional heterometallic Fe^{III}-Mn^{III} anionic single chain complex, the magnetic susceptibility for complex **1** has been simulated with the following Hamilton:

$$\hat{H} = \hat{H}_{ex} + \hat{H}_{anis} + g\beta H\hat{S}$$

The first term deal with the isotropic interactions (the magnetic couplings across the single cyanide bridge) and the contribution from the free high-spin Mn(III) ion. The second term corresponds to the local anisotropy of the high-spin manganese(III) ion, and the third term is the Zeeman interaction. As can be found from the crystal data, the two Fe(III)-CN-Mn(III) linkages are not with marked difference with the two Mn-N≡C bond angles of 157.1(3) and 151.5(3)°, respectively. Therefore, the compound **1** can be considered as a chain containing alternating spins 1/2 and 2 with approximately one exchange interactions J and the isolated spin 2 (Scheme 2). In this case, the magnetic susceptibilities of the infinite chain can be simulated and calculated rationally based on a closed ring cluster model consisting of four pairs of 1/2-2 spin pairs and plus four isolated Mn(III) ions (S = 2).



Scheme 2. Model used to analyse the magnetic data of complexes **1** and **2**.

The simulate was carried out through numerical matrix diagonalization techniques by using a Fortran program.[54] The best-fit parameters J = -7.36 cm^{-1}, D = -1.52 cm^{-1}, g = 1.99, R = 1.64×10^{-5}. This result, which is comparable to those found in other *mer*-cyanideiron(III)-based Fe(III)-Mn(III) complexes,[39b, c] further confirm the antiferromagnetic coupling between the cyanide-bridged $Fe^{III}Mn^{III}$, which is consistent with the fact that there usually exist antiferromagnetic interaction in *mer*-tricyanideiron-based Fe(III)-Mn(III) complexes.[39]

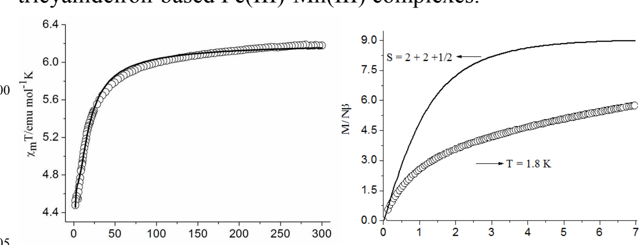


Figure 5. Temperature dependence of $\chi_M T$ (left, the solid line represents the best fit based on the parameters discussed in the text) and Field dependence of magnetization at 2 K of complex **1** (right).

The field-dependent magnetization measured up to 70 kOe at 1.8 K for complex **1** is shown in Figure 5. The magnetization increases with a relatively fast speed with increasing field until 15 kOe, then increases smoothly up to about 5.73 $N\beta$ until 70 kOe. This data is obviously lower than the saturated value of 9.0 $N\beta$ for the two uncoupled Mn(III) and one low spin Fe(III) based on g = 2.0, confirming again the antiferromagnetic coupling interaction between Fe(III) and Mn(III) ions bridged by cyanide group. The magnetization of 5.73 $N\beta$ at 70 kOe is also lower than the saturated value 7.0 $N\beta$ for the antiferromagnetic coupled Fe(III) and Mn(III) ion by plus one isolated Mn(III) ion, which can maybe be attributed to the zero-field spitting effect of the Mn(III) ion. The ac magnetic susceptibility of complex **1** performed in a 2 Oe ac field, with a zero dc field, Figure S6, shows no maximum and frequency dependence with the temperature down to 1.8 K, indicating that there is no magnetic ordering behaviour for this complex.

Table 2. Comparison of the magnetic property of cyanide-bridged Fe(III)-Mn(III) complexes based-on *mer*-tricyanideiron(III) building blocks.

compounds	Struct.	Mn-N$_{CN}$ (Å)	Mn-N≡C (°)	F/ AF	Ref.
[Mn(salen)][Fe(pzcq)(CN)$_3$]	1D	2.288(3) 2.263(3)	152.2(3) 158.3(3)	AF	39a
[Mn(salcy)][Fe(mpzcq)(CN)$_3$]	1D	2.287(5) 2.298(5)	169.1(4) 154.3(5)	AF	39b
[Mn(salen)][Fe(mpzcq)(CN)$_3$]	di-	2.275(3)	164.1(2)	AF	39b
[Mn((*R,R*)-Salcy)][Fe(pcq)(CN)$_3$]	1D	2.279(7) 2.275(7)	153.0(7) 166.4(7)	AF	47
[Mn((R,R)Salcy)][Fe(bpca)(CN)$_3$]	1D	2.3132(16) 2.3440(15)	147.69(15) 147.78(14)	AF	46
[Fe(iqc)(CN)$_3$][Mn(salen)]	1D	2.315(3) 2.273(3)	174.1(3) 167.1(3)	F	39d
[Fe(iqc)(CN)$_3$][Mn(5-Fsalen)]	1D	2.313(4) 2.281(4)	141.6(3) 151.4(3)	AF	39d
[Fe(iqc)(CN)$_3$][Mn(5-Clsalen)]	1D	2.260(7) 2.278(7)	155.2(8) 154.2(7)	AF	39d
[Fe(iqc)(CN)$_3$][Mn(5-Brsalen)]	1D	2.269(4) 2.265(4)	156.4(4) 147.6(3)	AF	39d
[Fe(pcq)(CN)$_3$Mn(saltmen)(CH$_3$OH)]	di	2.258(3)	153.2(2)	AF	40a
[Fe(bpca)(CN)$_3$Mn(3-MeO-salen)]	di	2.298(2)	146.09(18)	AF	40a
[Fe(bpca)(CN)$_3$][Mn(salpen)]	1D	2.360(2) 2.324(2)	144.24(18) 151.70(18)	AF	40a
[Fe(bpca)-(CN)$_3$][Mn(saltmen)]	1D	2.302(7) 2.337(6)	152.8(6) 153.8(7)	AF	40a
[Fe(bpca)(CN)$_3$Mn(5-Me-saltmen)]	1D	2.371(4) 2.314(4)	162.7(3) 169.7(3)	F	40a
[Fe(pcq)(CN)$_3$Mn(5-Me-saltmen)]	1D	2.366(4) 2.305(4)	160.9(4) 169.4(4)	F	40a
{Mn(salen)}$_2${Fe(qcq)(CN)$_3$}$_2$	1D	2.249(3) 2.319(2)	155.9(2)- 166.8(2)	AF	40b
{Mn(salpn)}$_2${Fe(qcq)(CN)$_3$}$_2$	1D	2.242(4)- 2.319(4)	166.6(3)- 172.7(3)	AF	I40b
[Mn(5-CH$_3$)salen][Fe(qcq)(CN)$_3$]	1D	2.269(5)- 2.334(5)	151.2(5)- 160.2(5)	AF	40c
[Mn(acphen)][Fe(qcq)(CN)$_3$]	1D	2.270(5)- 2.277(5)	159.1(5)- 161.5(5)	AF	40c
[Fe(qcq)(CN)$_3$][Mn(3-MeOsalen)]	di	2.287(3)- 2.289(3)	144.6(2)- 151.3(3)	AF	39c
[Fe(qcq)(CN)$_3$][Mn(5-Clsalen)]	1D	2.280(3)- 2.285(3)	147.7(3)- 161.4(3)	AF	39c
[Fe(qcq)(CN)$_3$][Mn(5-Brsalen)]	1D	2.283(6)- 2.291(5)	147.7(5)- 159.9(5)	AF	39c
Fe(qcq)(CN)$_3$][Mn(salen)]	1D	2.297(5)- 2.298(5)	149.3(5)- 153.5(5)	AF	39c

As revealed by Migule's group, two important factors can be mainly responsible for the magnetic coupling nature and strength in cyanide-bridged Fe(III)-Mn(III) system. The first factor defines the magnetic orbital of low spin Fe(III) center with $t_{2g}^5e_g^0$ electronic configuration, which can be used to describe its unpaired electron but sensitive to the electronic effects induced by its surrounding, and the second one is the value of the Mn-N≡C angle involving the cyanide group(s) that connect the manganese and iron centers. The magnetic orbital on the low-spin Fe(III) center ($d_{xy}/d_{xz}/d_{yz}$) has been proven with close relation to the number and the position of the cyanide groups around the Fe(III) ion by the above group through DFT calculation.[55] The $[FeL(CN)_4]^-$ (L = bidentate chelating ligand) types cyanide precursors often prefer a d_{xy} magnetic orbital, which can usually result in a weak ferromagnetic coupling between the cyanide-ridged Fe-Mn almost independent on the Mn-N≡C angle due to the non possibility of localizing any significant spin density on the cyanide bridge. For the cyanide-bridged Fe(III)-Mn(III) systems based-on $[Fe(CN)_6]^{3-}$ or *fac*-tricyanideiron(III) precursors, the magnetic coupling nature and strength are somewhat complicated, because all three t_{2g} orbitals can contribute in the same way to build the magnetic orbital. As for *mer*-tricyanideiron(III) types building blocks, the unpaired electron of the low-spin iron(III) center is defined by the d_{xz} type magnetic orbital, therefore making it possible delocalizing the electron density on the π-pathway of the cyanide ligand, in particularly on the cyanide-nitrogen atom that is coordinated to the manganese(III) ion. The four unpaired electrons of high-spin Mn(III) involved in elongated octahedral geometry are with the $\{(dxz,\ dyz,\ dxy)^3(dz^2)^1\}$ electronic configuration. Because of the orthogonality or overlap of the magnetic orbitals, their interaction with the d_{xz} magnetic orbital of Fe(III) ion through the single cyano bridge can lead to one antiferro- and three ferromagnetic contributions. Considering the stronger delocalization (σ-pathway) of the spin density from the Mn(III) occurring on the cyanide group, the ferromagnetic contribution from d_{xz}(Fe)-dz^2(Mn) dominates the other three ones i.e. d_{xz}(Fe)-d_{xz}(Mn), d_{xz}(Fe)-d_{xy}(Mn) and d_{xz}(Fe)-d_{yz}(Mn). Obviously, the bending of the Mn-N≡C angle affect the orthogonality of the magnetic orbitals and results in the relation: the smaller of the Mn-N≡C angle, the less orthogonality of the magnetic orbitals. As a result, the magnetic coupling nature between the cyanide-bridged Fe(III)-Mn(III) change from ferromagnetic to antiferromagnetic once the Mn-N≡C angle decreases to some extent. As summarized in Table 2, the antiferromagnetic coupling are common in the reported cyanide-bridged Fe(III)-Mn(III) complexes based-on *mer*-tricyanideiron(III) building blocks with very few exceptions containing the big Mn-N≡C angle(s). Meanwhile, it should be pointed out that the torsion angle (ϕ) defined as the rotation of the *x* and *z* axes for Mn(III) compared with the *xz* plane for Fe(III) can also play a role for the overlap of the magnetic orbitals, therefore sometime further mediating the Fe(III)-Mn(III) magnetic coupling through cyanide bridge.[56]

The magnetic properties of complexes 3 and 4.

The temperature dependence of magnetic susceptibility for compound $K_4[Fe_2(tbbp)(CN)_6]$, complexes **3** and **4** measured in the range of 2-300 K under an external magnetic field of 2000 Oe are illustrated in Figure S7, Figure 6 and S8 (ESI), respectively. The $\chi_M T$ value 0.43 emu K mol^{-1} for the cyanide precursor at room temperature is higher than the low-spin Fe(III) value of 0.375 K mol^{-1}, which can be attributed to the spin-orbital coupling and also indicate that there has no obvious magnetic interaction between the two low-spin Fe(III) ions through the bipyridine moiety. With the temperature lowering, the $\chi_M T$ value decreases very smoothly up to about 50K, and then decreases sharply and reaches the value of about 0.21 emu K mol^{-1} at 2 K. As shown in Figure 6, the $\chi_M T$ value at room temperature is about 0.847 emu K mol for complex **3**, slightly larger than the spin-only value of 0.75 emu K mol^{-1} expected for isolated Cu^{II} and low spin Fe^{III} (S = 1/2) centers assuming g = 2.0. With lowering the temperature, the $\chi_M T$ value decreases gradually to about 0.14 emu K mol^{-1} at 2K, suggesting the antiferromagnetic coupling between the cyanide-bridged Fe(III) and Cu(II) ion. The similar $\chi_M T$-T change tendency with almost linear confirmation could also be found in another cyanide-bridged Fe(III)-Cu(II) polymer,[57] which showed antiferromagnetic coupling between the low spin Fe(III) ion and Cu(II) ion through the bridging cyanide groups.

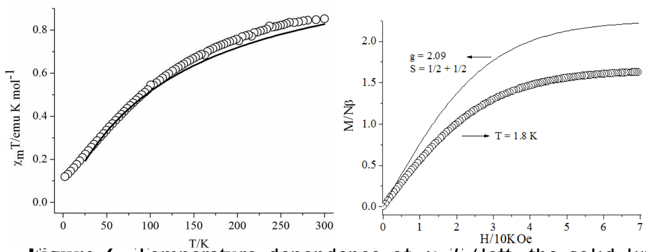


Figure 6. Temperature dependence of $\chi_M T$ (left, the solid line represents the best fit based on the parameters discussed in the text) and Field dependence of magnetization at 2 K of complex **3** (right). The calculated curves are based-on S_{Fe} = 1/2, S_{Cu} = 1/2 and g = 2.09.

The X-ray analysis of the ladder-like double chain structure of complexes **3** and **4** reveals two types of exchange paths, namely the adjacent Cu(II) and Fe(III) ions through the bridging cyanide group as well as the path between the low-spin Fe(III) ions through the conjugated bipyridine ligand. Considering that there has no obvious magnetic interaction between the two Fe(III) centers through bipridine moiety in these two complexes, complexes **3** and **4** can be approximatively treated as a single chain from the view point of the magnetism. Therefore, a uniform chain model based on the following spin Hamiltonian is suitable for evaluating the intra-chain coupling for complexes **3** and **4**:[58]

$$\hat{H} = -J\hat{S}_{Fe}\hat{S}_{Cu}$$

$$\chi_m = \frac{Ng^2\beta^2}{kT}\left[\frac{0.25+0.074975Y+0.075235Y^2}{1.0+0.9931Y+0.172135Y^2+0.757825Y^3}\right]$$

$$Y = \frac{|J|}{kT}$$

The data of the experiment $\chi_M T$ value of 20-300 K was used for fitting, giving the fitting parameters J = -4.35 cm^{-1}, g = 2.09, R = 2.42×10^{-4}. These results further confirm the antiferromagnetic coupling between the cyanide-bridged Fe(III) and Cu(II) ions in these two complexes. However, no acceptable fitting results can be obtained for the low temperature magnetic data (2-20 K) even if the interchain supramolecular magnetic interactions (zJ') were introduced in the model in the mean field approximation. The existence of antiferromagnetic coupling in complex **3** is also supported by the isothermal magnetization measurements at 1.8 K, as shown in Figure 6. The calculated curve lies above the experimental data, indicating also the presence of appreciable antiferromagnetic interaction in complex **3**.

As described above, due to the strict orthogonality of the magnetic orbitals, the observed ferromagnetic coupling between nearest paramagnetic neighbours in linear cyanide-bridged systems can be commonly found. The copper(II) ion is a Jahn-Teller-active metal ion with the electronic configuration $t_{2g}^6e_g^3$ and tends to afford short, strong equatorial bonds and long, weak bonds to the terminal N atoms of the bridging cyanide ligands. Therefore, the universal ferromagnetic coupling observed in cyanide-bridged Fe(III)-Cu(II) examples can be easily interpreted by the orthogonality of the t_{2g} magnetic orbitals of Fe(III) ion with the e_g one of Cu(II) ion. However, despite the existing of the usual ferromagnetic interaction, several cyanide-bridged Fe(III)-Cu(II) complexes presented antiferromagnetic coupling.[57,59-60] Similar to the analysis above, the bending of the Cu-N≡C angle and the rotation torsion angle (ϕ) are also important for tuning the coupling nature and strength between the cyanide-bridged Fe(III)-Cu(II),[61] since they can remove the strict orthogonality of the t_{2g} and e_g orbital on iron(III) and copper(II) ions. Previous study on cyanide-bridged Fe(III)/Cr(III)-Ni(II) systems, in which the ferromagnetic coupling could be universally observed, showed that the strength of the ferromagnetic coupling between the Fe(III)/Cr(III) and Ni(II) through cyanide linkage became weaker with the value of the Fe/Cr-C≡N-Ni(II) angle decreasing, and even changed to antiferromagnetic coupling when this angle lower than about 145°.[62] Investigation of the structural parameters of the reported cyanide-bridged Fe(III)-Cu(II) complexes, one can found that those ones exhibiting ferromagnetic coupling are always with comparative bigger Cu-N≡C bond angle(s) and the rare example $[Cu(1,3\text{-}Pn)_2]_2[Fe^{III}(CN)_6]ClO_4\cdot 2H_2O$ (1,3-Pn = 1,3-diaminopropane) showing obvious antiferromagnetic interaction between cyanide-bridged Fe(III)-Cu(II) is with small Cu-N≡C bond angle.[57] The Cu-C≡N bond angles in the present complex are very far from a linear configuration with the values about 130°, which is even smaller than that in the above reported complex. Such the small Cu-N≡C angles and the additional role from the rotation torsion angle (ϕ) can seriously affect the orbital orthogonality, and making maybe the presence of an overlap of magnetic orbitals of the Fe(III) and Cu(II) possible. Unfortunately, no more antiferromagnetic coupled Fe(III)-Cu(II) examples can be used for comparison, therefore the antiferromagnetic coupling nature between the cyanide-bridged Fe(III)-Cu(II) is still an open question at present.

Conclusion

In summary, by using *mer*-cyanideiron(III) precursors as building blocks and chiral manganese(III)/copper(II) compounds as assemble segments, a pair of cyanide-bridged single chain chiral enantiopures and a pair of ladder-like double chain chiral enantiopures have been synthesized and structurally characterized. Circular dichroism (CD) spectra confirm the enantiomeric nature of the optically active complexes. Investigation over the magnetic properties of the four complexes show that antiferromagnetic couplings are operative both between Fe^{III}-Mn^{III} and Fe^{III}-Cu^{II} centers bridged by CN group(s). The present result and the one reported recently[52] indicated that the this types of *mer*-cyanideiron(III) precursors were good candidates for assembling low dimensional cyanide-bridged heterometallic complexes, especially for one-dimensional system. Synthesis and magnetic investigation over other series of cyanide-bridged heterometallic 1D complexes based-on the above building blocks, especially for the using of the newly bimetallic cyanide precursor, with interesting magnetic properties, in particular single chain magnet nature, by employing appropriate spin carriers are under way in our laboratory.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Crystallographic data in CIF format. The MCD spectra of complexes **1** and **3**. The perspective view of ladder-like double infinite chains of **3** (S,S isomer, left) and **4**(R,R isomer, left). The cell packing diagram along *a* axis of complexes **3** and **4**. Temperature dependence of $\chi_M T$ the compound $K_4[Fe_2(tbbp)(CN)_6]$, complexes **2** and **4**. The ac magnetic susceptibility of complex **1**. Selected bond lengths and angles for complexes **1**-**4**. See DOI: 10.1039/b000000x/

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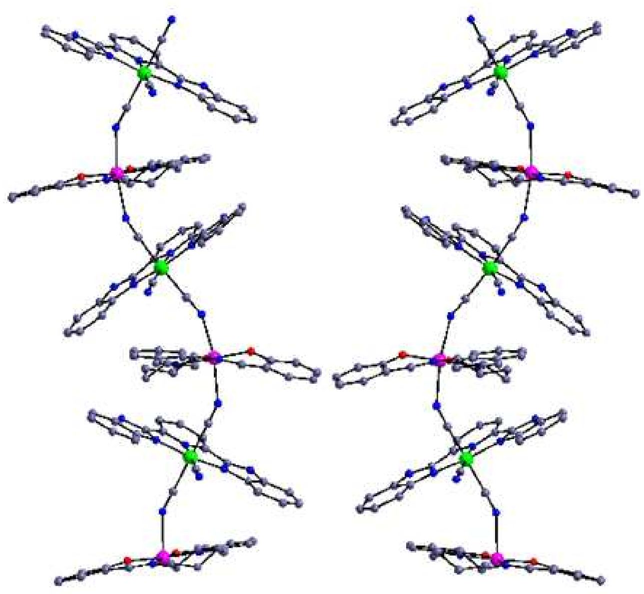
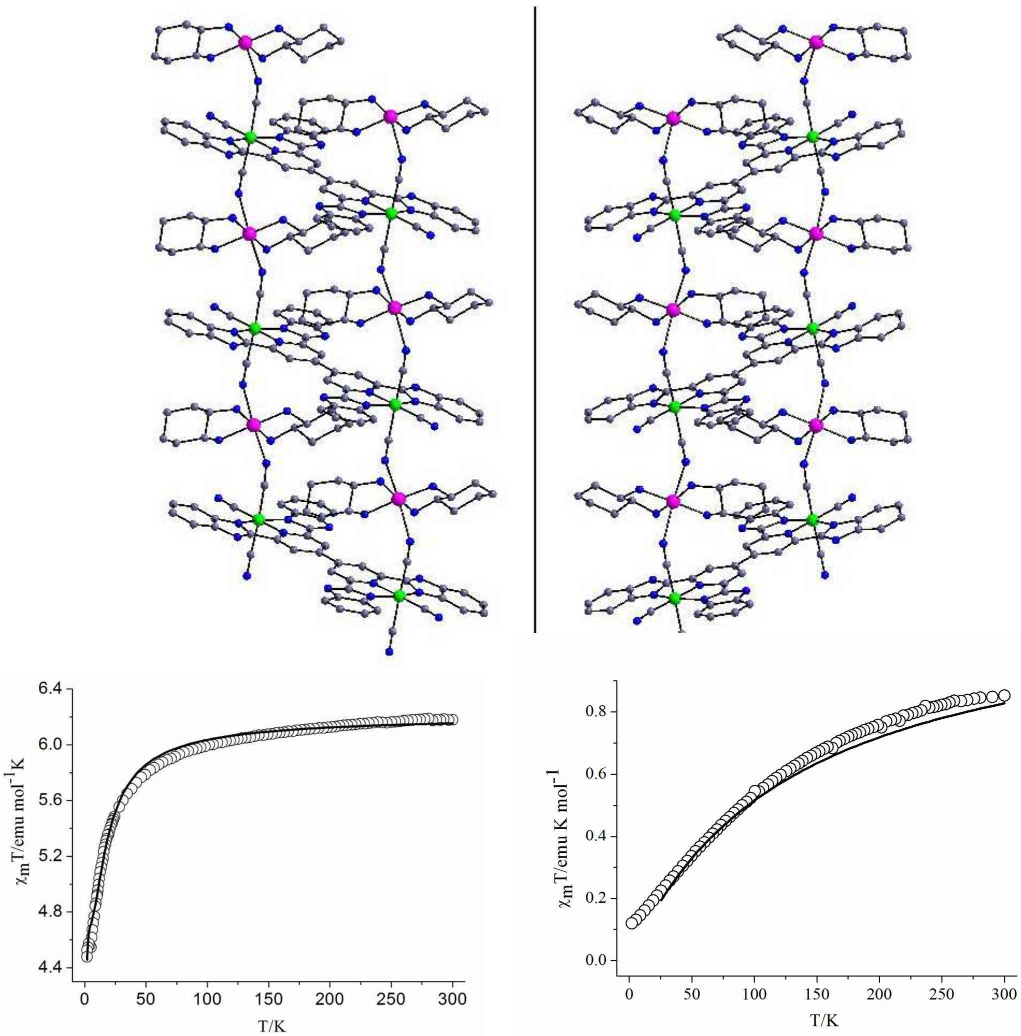
Graphical Abstract:

Synthesis, Crystal Structures and Magnetic Properties of *mer*-Cyanideiron(III)-Based 1D Heterobimetallic Cyanide-Bridged Chiral Coordination Polymers

Daopeng Zhang,[a,b] Shuping Zhuo,[a,*] Hongyan Zhang,[a] Ping Wang,[a] and Jianzhuang Jiang[b,*]

Two pairs of cyanide-bridged heterometallic chiral enantiomer complexes structurally characterized as infinite chain have been successfully assembled from two *mer*-iron(III) building blocks $[PPh_4]_2[Fe(bbp)(CN)_3]$, $K_4[Fe_2(tbbp)(CN)_6]$ and four chiral manganese(III)/copper(II) compounds, characterized by elemental analysis, IR spectroscopy, circular dichroism (CD) and magnetic circular dichroism (MCD) spectrum and magnetically investigated.





$\chi_m T$/emu mol^{-1}K
6.4
6.0
5.6
5.2
4.8
4.4
0 50 100 150 200 250 300
T/K
$\chi_m T$/emu K mol^{-1}
0.8
0.6
0.4
0.2
0.0
0 50 100 150 200 250 300
T/K