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The supramolecular interaction mediated chiral 1D cyanide-bridged metamagnet: synthesis, crystal structures and magnetic properties

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Two cyanide-bridged enantiopure one-dimensional single chain complexes, $[\text{Mn}((R,R)\text{-Salcy})\text{Fe}(\text{pcq})(\text{CN})_3]_{2n} \cdot 1.5\text{nDMF}$ (**1**) and $[\text{Mn}((S,S)\text{-Salcy})\text{Fe}(\text{pcq})(\text{CN})_3]_{2n} \cdot 1.5\text{nDMF}$ (**2**), have been synthesized and structurally characterized. Systematically magnetic investigations show the antiferromagnetic coupling between the cyanide-bridged Mn(III)-Fe(III) centers and the interesting metamagnetic behavior at about 5.0K resulted from the intermolecular π - π interaction.

Due to the excellent magnetic transferring ability of cyanide group and their relatively readily controlled and predicted molecular topological structures, cyanide-bridged magnetic complexes, especially those multifunctional molecule-based magnetic materials, such as photomagnets, magneto-optical materials, magnetic conductors, ferroelectromagnets and chiral magnets, have attracted increasing interest over the past three decades. In particular, the design and synthesis of chiral magnets is of great interest for fundamental investigations on the magnetization-induced second harmonic generation (MSHG) and magneto-chiral dichroism (MChD), and their possible applications in a variety of new technologies¹⁻⁶. However, despite many previous efforts, the rational preparation of chiral cyanide-bridged molecular magnetic material is still a challenge because the chirality must be controlled in the molecular structure as well as in the entire crystal structure⁷⁻¹¹.

Recently, several cyanide-bridged chiral magnetic complexes have been successfully synthesized with poly-cyanometalates or modified multi-cyanometalates as bridging units and unsaturated transition-metal complexes containing chiral coligands as assemble segments^{11, 12-15}. To extend new low-dimensional cyanide-bridged homochiral heterobimetallic compounds with interesting magnetic properties such as SMMs and SCMs and other physical properties, and also for the purpose of further elucidating the magneto-structural correlation, we choose anionic $\text{mer-}[\text{Fe}^{\text{III}}(\text{pcq})(\text{CN})_3]^-$ ($\text{pcq} = 8\text{-}(\text{pyridine-2-carboxamido})\text{quinoline anion}$) and the cationic chiral Schiff-base manganese compounds with strong uniaxial magnetic anisotropy due to the Jahn-Teller effect of the six-coordinated Mn^{III} ion to assemble chiral cyanide-bridged magnetic complexes. The cyanide precursor $\text{mer-}[\text{Fe}^{\text{III}}(\text{pcq})(\text{CN})_3]^-$ developed firstly by our group to prepare cyanide-bridged system and its analogues have been proved suitable building blocks for the assembling of low-dimensional heterometallic cyanide-bridged magnetic complexes¹⁶⁻¹⁸. In this paper, we report the design, synthesis, crystal structures and detailed magnetic properties of two enantiomerically pure chiral cyano-bridged heterobimetallic chain coordination polymers, $[\text{Mn}((R,R)\text{-Salcy})\text{Fe}(\text{pcq})(\text{CN})_3]_{2n} \cdot 1.5\text{nDMF}$ (**1**) and $[\text{Mn}((S,S)\text{-Salcy})\text{Fe}(\text{pcq})(\text{CN})_3]_{2n} \cdot 1.5\text{nDMF}$ (**2**) ($\text{Salcy} = \text{N}, \text{N}'\text{-}(1,2\text{-cyclohexanedilethylene})\text{bis}(\text{salicylideneiminato})\text{ dianion}$, $\text{pcq} = 8\text{-}(\text{pyridine-2-carboxamido})\text{quinoline anion}$). It is worth noting, to our best of the knowledge, reports on chiral cyanide-bridged

complexes assembled from chiral Schiff-base manganese compounds are still limited¹¹, despite of the fact that numerous Schiff-bases based cyanide-bridged systems with diverse structures have been synthesized¹⁹. Interestingly, systematically investigation over the magnetic properties of the two chain complexes reveals some characters of metamagnet behavior at low temperature due to the relatively strong interchain π - π interaction. This work may provide information for the understanding and application of supramolecular interaction in the molecular magnetic materials.

The stoichiometric reactions of $\text{mer-}[\text{PPh}_4][\text{Fe}(\text{pcq})(\text{CN})_3]$ and $[\text{Mn}((R,R)\text{-Salcy})(\text{H}_2\text{O})(\text{C}_2\text{H}_5\text{OH})]\text{ClO}_4$ or $[\text{Mn}((S,S)\text{-Salcy})(\text{H}_2\text{O})(\text{C}_2\text{H}_5\text{OH})]\text{ClO}_4$, which have also been structurally characterized (Fig. S1 and Table S1, ESI), with a 1:1 molar ratio under room temperature afforded dark brown crystals of complexes **1** and **2** with the yield about 60% (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 (Figs.1 and 2) and magnetic property investigation. Single X-ray diffraction analysis reveals that complex **1** structurally characterizes as neutral linear zigzag single chains consisting of the asymmetric chiral unit of $\{[\text{Mn}((R,R)\text{-Salcy})\text{Fe}(\text{pcq})(\text{CN})_3]\}_2$ (Fig. 1). Within the chain of complex **1**, each $\text{mer-}[\text{Fe}^{\text{III}}(\text{pcq})(\text{CN})_3]^+$ acting as bidentate ligand binds two $[\text{Mn}((R,R)\text{-Salcy})]^{2+}$ by using its two *cis* cyanide groups, therefore forming a "Z"-like chain conformation. The coordination sphere of Mn(III) ion is an elongated octahedral geometry (Table S2, ESI), typical of the Jahn-Teller effect along the $\text{N}_{\text{cyanide}}\text{-Mn-N}_{\text{cyanide}}$ axis, with the four equatorial positions are occupied by N_2O_2 unit from Schiff-base ligand and the other two axial ones resulting from N atoms of the bridging cyanide groups, which can be testified by the coordination parameter around the Mn(III) ion (Table S2, ESI). Comparable to the Fe-C \equiv N angles with the values very close to 180°, the Mn-N \equiv C bond angles are only about 166.4(7) and 153.0(7)°, respectively, which are slightly larger than those found in others 1D cyanide-bridged Fe-Mn complexes^{20, 11a}, indicating that these three atoms are obviously away from a linear configuration. The chains are running along the *c* axis with the intrachain Fe-Mn separation through bridging cyanide 5.207 Å. The nearest inter-chain metal-metal distances between the neighboring chains along the *b* axis is 8.227 Å, markedly longer than the intrachain metal-metal distances. It is worth noting that the one-dimensional chains are linked by π - π interactions with the distance 3.821 Å between aromatic rings of pcq ligand, leading to a two-dimensional architecture (Figs. S2 and S3, ESI).

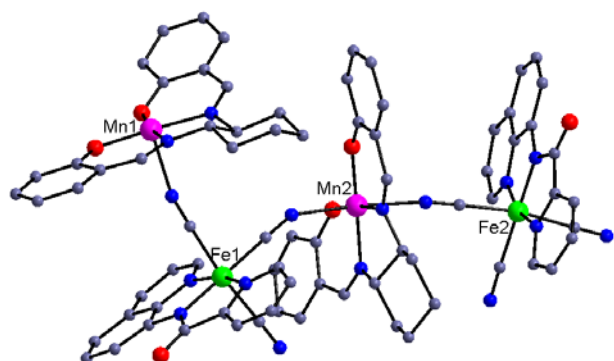


Fig. 1. Perspective drawing of the crystallographically structural unit of **1** showing the atom numbering. H atoms and the solvent molecules are omitted for clarity.

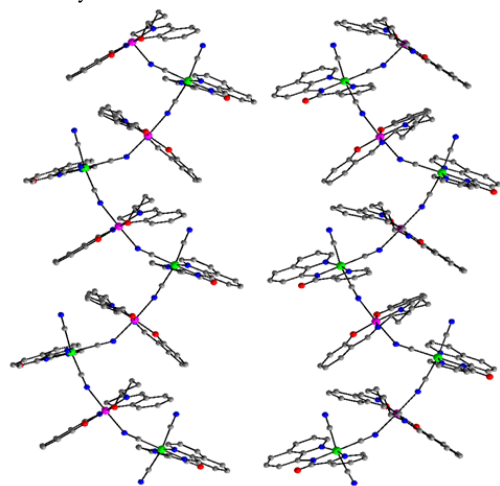


Fig. 2. Perspective view of one-dimensional zigzag infinite chains of **1** (R,R isomer, left) and **2** (S,S isomer, right), respectively.

The circular dichroism (CD) spectrum measurements in KBr pellets further confirm the optical activity and enantiomeric nature of complexes **1** and **2**. The CD spectrum of **1** (*R* isomer) exhibits a positive Cotton effect at λ_{max} 315, 353, and 396 nm, while **2** (*S* isomer) shows Cotton effects of the opposite sign at the same wavelengths (Fig. S4, ESI). The Magnetic circular dichroism (MCD) spectra were recorded on a JASCO-815 spectrodichromometer equipped with a JASCO electromagnet, which produces magnetic fields of 1.60 T with both parallel and antiparallel fields. The magnitudes ($[\theta]_{\text{M}}$) were expressed in terms of molar ellipticity per tesla ($\text{deg dm}^3 \text{mol}^{-1} \text{cm}^{-1} \text{T}^{-1}$) (Fig. S5, ESI).

The temperature dependence of magnetic susceptibility for these two complexes was measured in the range of 1.8–300 K under the external magnetic field of 2000 Oe (Fig. 3 and Fig. S6, ESI). The $\chi_{\text{m}}T$ value per $\text{Fe}^{\text{III}}\text{Mn}^{\text{III}}$ unit at room temperature is $3.22 \text{ emu K mol}^{-1}$, which is slightly lower than the spin only value of $3.375 \text{ emu K mol}^{-1}$ for uncoupled Mn(III) ($S = 2$) and low spin Fe(III) ($S = 1/2$) based on $g = 2.00$. With decreasing the temperature, the $\chi_{\text{m}}T$ value decreases gradually and attains the value of $2.24 \text{ emu K mol}^{-1}$ at about 20 K, indicating the presence of antiferromagnetic coupling between the cyanide-bridged Fe(III)-Mn(III). After this, the $\chi_{\text{m}}T$ value starts to increase with a high speed and reaches its highest peak with the value about $2.86 \text{ emu K mol}^{-1}$ at 5 K, and then it decreases again to its lowest value $0.27 \text{ emu K mol}^{-1}$ at 1.8K. The trough behavior of $\chi_{\text{m}}T$ plot at about 20 K is typical of a ferrimagnetic behavior. The magnetic susceptibility conforms well to Curie-Weiss law in the high temperature range of 20–300 K and gives the negative Weiss constant -19.6 K and Curie constant $3.40 \text{ emu K mol}^{-1}$,

demonstrating further the presence of antiferromagnetic alignments between spin centers.

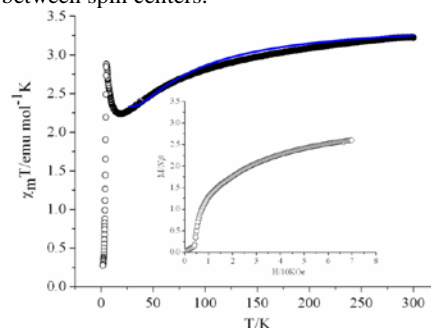


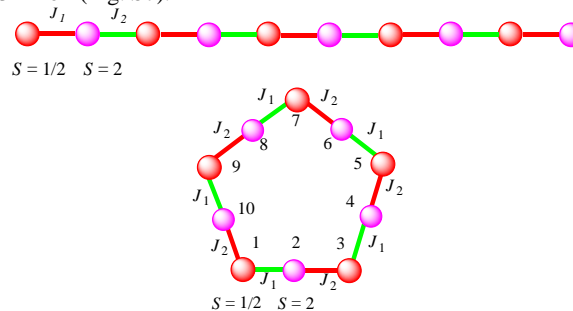
Fig. 3. Temperature dependence of $\chi_{\text{m}}T$ of complex **1** (the blue solid line represents the best fit based on the parameters discussed in the text). Inset: Field dependence of magnetization at 1.8 K.

As can be found from the crystal data, the two Fe(III)-CN-Mn(III) linkages is unequal with the two Mn-N≡C bond angles $166.4(7)$ and $153.0(7)^\circ$, respectively. A regular chain model is not suitable for evaluating the intrachain couplings. As a consequence, the Seiden model (the alternating chain model) of quantum spins ($S_i = 1/2$ for Fe^{III} ion) and classical spins ($S_i = 2$ for Mn^{III} ion) based on the following spin Hamiltonian was employed²¹.

$$H = -2J \sum_{i=1}^N (S_i + S_{i+1}) S_i$$

Considering that the effects resulted from the intermolecular interaction and the zfs (zero-field splitting) of Mn(III) ion are relatively small and can therefore be safely neglected at comparable high temperature, the data of the experiment $\chi_{\text{m}}T$ value of 20–300 K was used for fitting, giving the best-fit parameters $J = -8.67 \text{ cm}^{-1}$, $g = 2.05$, $R = 5.34 \times 10^{-5}$.

To further analyze the magnetic data of this one-dimensional heterometallic $\text{Fe}^{\text{III}}\text{-Mn}^{\text{III}}$ single chain complex, the magnetic susceptibility for complex **1** has been simulated by using MAGPACK program²². According to the reported method²², the compound **1** can be considered as isotropic Heisenberg chain containing alternating spins $1/2$ and 2 with two antiferromagnetic exchange interactions J_1 and J_2 (Scheme 1), for which is based on the two kinds of CN- bridges. In this case, the magnetic susceptibilities of the infinite single chain can be simulated and calculated rationally satisfactorily based on a closed ring cluster model consisting of five pairs of $1/2$ - 2 spin pairs with two alternating antiferromagnetic exchange interactions J_1 and J_2 , Scheme 1. The best least-squares fit between 20–300 K yields $J_1 = -12.35 \text{ cm}^{-1}$ and $J_2 = -2.35 \text{ cm}^{-1}$, $g = 2.008$, $R = 1.34 \times 10^{-5}$ (Fig. S7).



The results confirm the presence of antiferromagnetic interactions between the cyanide-bridged Mn^{III} and Fe^{III} ions, which is different from the fact that most of the cyanide-bridged Fe(III)-Mn(III) complexes can exhibit ferromagnetic properties. It has been improved that ferromagnetic or antiferromagnetic

coupling could be found between the cyanide-bridged low-spin Fe(III) and high-spin Mn(III) because of the strict orthogonality of the magnetic orbitals ($[d_{xy}/d_{xz}/d_{yz}]^1$ in Fe^{III} vs. $d_{z^2}^1$ in Mn^{III}) and the orbital overlap between d_{xz} , d_{yz} , d_{xy} orbitals of Fe^{III} and Mn^{III}. Although the orbital orthogonality effect, which can result in ferromagnetic coupling, usually overwhelms the orbital overlap effect, the frequent bending of the Mn–N≡C–Fe linkages and the rotation of the x and z axes for Mn(III) should enlarge the overlap^{20, 23}, therefore weaken the ferromagnetic contribution and sometime gave rising to antiferromagnetic coupling between the cyanide-bridged Fe(III)–Mn(III) centers.

The field dependent magnetization for complex **1** was measured up to 50 kOe at 1.8 K (insert of Fig. 3) and 5 K (Fig. S8, ESI). Different from that at 5K, the curve at 1.8K present a sigmoid shape, typical of metamagnetic behavior: The magnetization first increases slowly with increasing magnetic field until 5 kOe due to the relatively strong intermolecular π - π interaction, then increases abruptly for a phase transition, and finally attains their highest value about $2.5 N\beta$ at 60 kOe. To confirm the magnetic phase transition at low temperature, the field cooled magnetization (FCM) curves were measured under different magnetic fields in the range of 1.8–30 K (Fig. 4). Below 4 kOe, the FCM curves show a peak at about 5.0 K, which can be considered as the phase transition temperature. The absence of a peak at 10 kOe confirms the metamagnetic behavior of complex **1** at low temperature. The ac magnetic susceptibility performed in a 2 Oe ac field, with a zero dc field, Fig. 5 shows the peak at about 5.0 K, indicating also its three-dimensional magnetic ordering behavior. Also, the ac magnetic susceptibility under dc field of 5 kOe, actually approximate the value of critical field (H_c) to overcome the intermolecular antiferromagnetic interaction, has been measured. The results show that both of the real part and imaginary part of the ac magnetic susceptibility have a peak about 3.3K, demonstrating the field-induced three-dimensional ferromagnetic magnetic ordering below this temperature due to the intermolecular antiferromagnetic interaction overcome by the increased dc field (Fig. S9, ESI). The magnetic ordering behavior is further supported by the hysteresis loop measured at 1.8 K (Fig. S10, ESI).

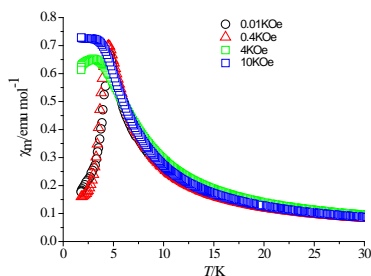


Fig. 4. Field-cooled-magnetization of complex **1** in applied fields of 0.01 kOe, 0.4 kOe, 4 kOe and 10 kOe.

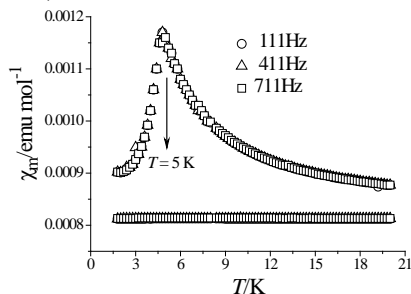


Fig. 5. Temperature dependence of ac magnetization of complex **1** in a zero-static field and an ac field of 2 Oe at frequencies of 111, 411 and 711 Hz.

In summary, by using *mer*-[PPh₄][Fe(pcq)(CN)₃] as building block and chiral Schiff-base manganese compounds as assemble segments, two cyanide-bridged enantiopure one-dimensional single chain complexes have been synthesized and structurally characterized. Circular dichroism (CD) spectra confirm the enantiomeric nature of the optically active complexes. Detailed magnetic studies show that antiferromagnetic couplings are operative between Fe^{III} and Mn^{III} centers bridged by CN group and their metamagnetic behavior at low temperature due to the intermolecular π - π interactions.

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Notes and references

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- † Electronic Supplementary Information (ESI) available: Crystallographic data in CIF format. The cationic crystal structures of the two schiff-base compounds. The cell packing diagram for complexes **1** and **2**. The π - π interactions between the adjacent chains. The MCD and CD spectra of the two complexes. The Temperature dependence of $\chi_m T$ of complex **2**. The temperature dependence of $\chi_m T$ fitting for complex **1** by using Magpack. The field dependent magnetization for complex **1** at 5K. The ac susceptibility of complex **1** under dc field of 5 kOe. Hysteresis loop for complex **1** 1.8 K. Selected bond lengths and angles for complexes **1** and **2**. The preparation procedure for complexes **1** and **2**. Details of crystal data collection and refinement strategy for the two complexes and the two starting schiff-base manganese compounds..
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