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From tetranuclear cluster with single-molecule-magnet behavior to 1D alternating spin-canting chain in a Fe(III)–Mn(III) bimetallic system

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ABSTRACT

A tetranuclear cluster and an alternating zigzag chain were synthesized via rational assembly of the same cyanometalate building blocks with different Mn(III) Schiff bases possessing varying proportions of sterically hindered groups causing steric hindrances. The tetranuclear cluster $[(Tp^*)Fe(CN)_3]_2[Mn(salen)]_2\cdot H_2O$ [**1**; $[(Tp^*)Fe(CN)_3]^-$ [Tp* = hydrotris(3,5-dimethylpyrazol-1-yl) borate], salen = N,N′-ethylenebis(salicylideneiminato) dianion] was formed with Schiff bases possessing smaller steric hindrances, whereas the one-dimensional alternating zigzag chain $\{[(Tp^*)Fe(CN)_3Mn(salcyen)]\cdot 2CH_3OH\cdot H_2O\}_n$ [**2**; salcyen = N,N′-(1,2-cyclohexanediylethylene) bis(salicylideneiminato) dianion] was formed with Schiff bases possessing larger steric hindrances. Magnetic measurements revealed that **1** exhibits single-molecule-magnet behavior with dominant ferromagnetic interactions, whereas **2** exhibits spin-canting behavior with dominant antiferromagnetic interactions.

In materials science research in recent years, molecule-based magnetic materials have attracted considerable attention from chemists, physicists, and biologists as a new type of soft material [1–4]. Among them, cyano-bridged bimetallic assemblies have been studied most extensively [5–8] because the cyanide ligand can effectively transmit magnetic interactions between paramagnetic centers [9]. In particular, the use of tricyanometalate $[LFe(CN)_3]^{n-}$ (where L = polydentate and N = donor chelating ligands) anions [10–14] to synthesize low-dimensional materials, such as single-molecule magnets (SMMs) and single-chain magnets (SCMs) [15–17] via rational designs utilizing the linear linkage mode along the C–N direction, has been thoroughly investigated.

Moreover, manganese(III) Schiff bases show strong uniaxial magnetic anisotropy as a result of inherent Jahn–Teller elongations [18] in axial directions, which is important for SMMs [19,20]. Several dimeric manganese(III) tetradentate Schiff base complexes have been reported with some exhibiting the characteristic SMM behavior [21]. We aimed to develop new low-dimensional materials by combining tricyanometalate $[Tp^*Fe(CN)_3]^-$ [Tp* = hydrotris(3,5-dimethylpyrazol-1-yl) borate] anions and Mn(III) Schiff bases, wherein the nitrogen atoms of cyano bridge are assumed to occupy the empty coordination sites in Mn(III) Schiff bases [22]. With this strategy, one tetranuclear cluster $[(Tp^*)Fe(CN)_3]_2[Mn(salen)]_2\cdot H_2O$ [**1**; $[(Tp^*)Fe(CN)_3]^-$, salen = N,N′-ethylenebis(salicylideneiminato) dianion] showing SMM behavior was synthesized when Schiff bases with smaller steric hindrances were used [23]. When Schiff bases [24] with larger steric hindrances were used, a one-dimensional alternating zigzag chain $\{[(Tp^*)Fe(CN)_3Mn(salcyen)]\cdot H_2O\cdot 2CH_3OH\}_n$ [**2**; salcyen = N,N′-(1,2-cyclohexanediylethylene)bis(salicylideneiminato) dianion], showing spin-canting was obtained.

Compound **1** is synthesized by a diffusion method [25] and obtained as black crystals. Single-crystal X-ray diffraction analysis [26] reveals that **1** crystallizes in a triclinic $P\bar{1}$ space group. As shown in Fig. 1(a), a tetranuclear compound is formed, wherein the two Mn(III) centers are linked by two phenoxides and capped by two $[(Tp^*)Fe(CN)_3]^-$ building blocks. Each Fe(III) center adopts a distorted octahedral geometry, consisting of three N atoms from Tp* and three C atoms from CN^- ligands. The Fe–C bond lengths are 1.915–1.935 Å and the Fe–N distances are 1.996–2.021 Å, respectively, in good agreement with those observed in other low-spin Fe(III) compounds [27]. Each Mn(III) center is located in the octahedral environment with two nitrogen and two oxygen atoms from salen ligands, one cyanide nitrogen atom from a $[(Tp^*)Fe(CN)_3]^-$ building block, and one oxygen atom from another Schiff base. The Mn(III) environment is a Jahn–Teller distorted octahedron with short equatorial (eq) Mn–N(O) bond lengths of $Mn-N_{eq}$ = 1.978 Å and $Mn-O_{eq}$ = 1.894 Å and with long apical (ap) $Mn-N_{ap}$ and $Mn-O_{ap}$ distances of 2.195 Å and 2.494 Å, respectively. The angles relevant to the phenoxide bridges are 85.61° for O–Mn–O, 99.54° for Mn–O–Mn, and 88.12° for N–Mn–O. The Mn–N–C angle in the cyano-bridged pathways is 154.6°. The intradimer distance between Fe(III) and Mn(III) centers is 5.063 Å.

Compound **2** crystallizes in a monoclinic $P2(1)/n$ space group. The crystal structure comprises alternating zigzag chains with uncoordinated

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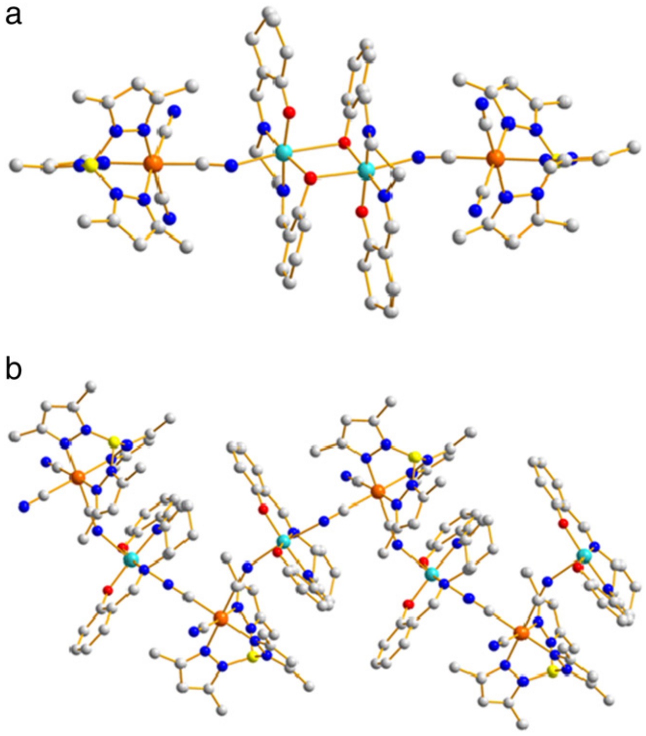

Fig. 1. (a) Tetranuclear structural unit of **1**. (b) Molecular view of complex **2** with the bimetallic chain structure. H atoms are omitted for clarity. Atomic scheme: Fe, orange, Mn, aqua, C, gray, N, blue, and B, yellow.

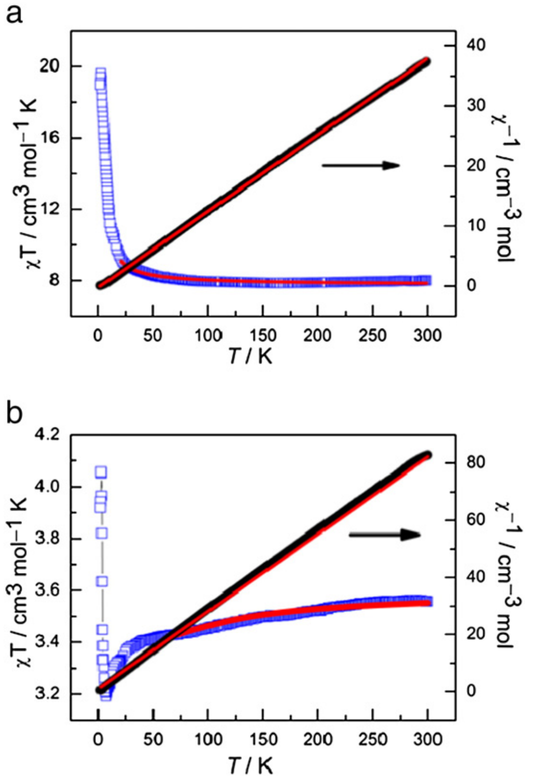

Fig. 2. (a) Temperature-dependent magnetic susceptibility for compound **1**. (b) Temperature-dependent magnetic susceptibility for compound **2**. The red solid line is the fitting to the Curie–Weiss law and magnetic models described in the text.

water and methanol molecules among them (see Fig. 1(b)). The Mn(III) ion is located in an elongated octahedral geometry; the equatorial plane is occupied by two nitrogen and two oxygen atoms from salcyen; and the apical position is occupied by two N atoms from the cyano bridge. The $\mathrm{Mn-N_{ap}}$ bond lengths are 2.2846 Å and 2.274 Å, respectively. The Fe – C bond lengths range from 1.924 to 1.944 Å, and the Fe – N distances range from 1.981 to 2.013 Å. Structural parameters indicate that the iron centers are $\mathrm{Fe^{III}}_{\mathrm{LS}}$. The bond angles are 151.50° for C – N – Mn and 173.47° for N – Mn – N, which are important for magnetic interactions.

As displayed in Fig. 2(a), the temperature-dependent magnetic susceptibility of **1** was measured under 1 kOe in a 2–300 K temperature range. At room temperature, the χT value is 8.17 $\mathrm{cm^3\ mol^{-1}\ K}$, in good agreement with the theoretical value of 8.16 $\mathrm{cm^3\ mol^{-1}\ K}$ of two low-spin Fe(III) ions and two high-spin Mn(III) ions, assuming $g_{\mathrm{Fe}} = g_{\mathrm{Mn}} = 2.2$. As the temperature decreases, the χT values remain nearly constant between 300 and 90 K and increase sharply and reach a maximum value of 19.61 $\mathrm{cm^3\ mol^{-1}\ K}$ at 11 K. This indicates the existence of dominant ferromagnetic interactions between spin centers. A small drop in χT below the cusp temperature is then associated with zero field splitting of a ground state and/or intermolecular antiferromagnetic interactions. The Curie–Weiss law [$\chi_m = C / (T - \theta)$] is applied to the temperature ranges of 2–300 K. Magnetic fitting indicates that the Weiss constant $\theta = 1.90$ K, with the positive value confirming that ferromagnetic interactions are dominant in the tetranuclear compound. In the temperature of 20–300 K, the MAGPACK [28] program based on the isotropic spin Hamiltonian $H = -2J_1(S_{\mathrm{Fe1}} \cdot S_{\mathrm{Mn1}} + S_{\mathrm{Mn2}} \cdot S_{\mathrm{Fe2}}) - 2J_2(S_{\mathrm{Mn1}} \cdot S_{\mathrm{Mn2}})$ is used to obtain the parameters $J_1 = 1.51\ \mathrm{cm^{-1}}$, $J_2 = 0.62\ \mathrm{cm^{-1}}$, $g = 2.14$ and $R = 8.2 \times 10^{-5}$. The fitting results further indicate the ferromagnetic coupling between the spin centers. Field dependence of magnetization for **1** at 1.8 K is shown in Fig. S1. As the applied magnetic field increases, the isothermal magnetization steeply increases to a value of 8.3 Nβ at 50 kOe.

To investigate the magnetization dynamic behavior, alternating current (ac) susceptibility measurements were studied at different frequencies (10–1000 Hz) in a 3.5 Oe ac field and zero direct current (dc) field. As shown in Fig. 3, obvious frequency-dependent in-phase components (χ') and out-of-phase ones (χ'') were observed for **1**, indicating a slow relaxation of the magnetization. Due to the absence of observed maxima of ac susceptibility signals, the Debye model is

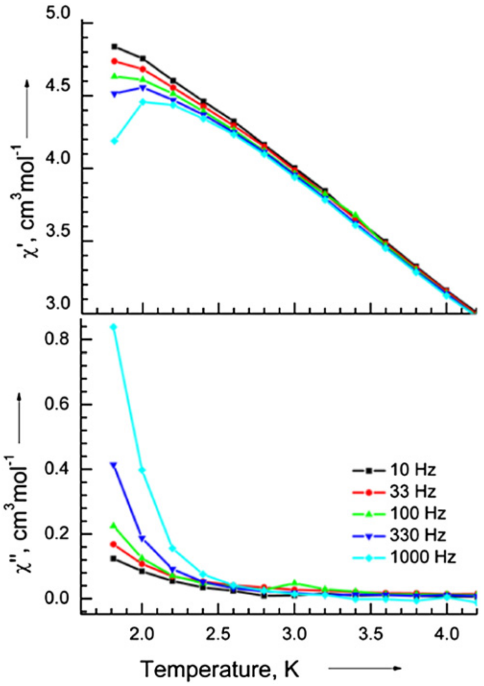

Fig. 3. Frequency dependence of ac magnetic signals of compound **1** at $H_{ac} = 3.5$ Oe and $H_{dc} = 0$ Oe.