Ferromagnetic Assemblies Composed of Mn^{III} Salen-Type Complexes and a Tripodal Fe^{III} Complex with an Imidazolate Bridge

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The use of a low-spin Fe^{III} complex bearing three imidazolate groups in a reaction with Mn^{III} salen-type complexes provided two different imidazolate-bridged Mn^{III}–Fe^{III} assemblies, a dinuclear complex and a one-dimensional chain, dependent on the salen ligand and counter ion used. Both compounds exhibit a ferromagnetic exchange between Mn^{III} and Fe^{III} centers via the imidazolate linkage.

The recent research for new molecular magnetic materials has led to stupendous progress especially in low-dimensional systems including single-molecule magnets (SMMs)[1] and single-chain magnets (SCMs),[2] which are expected to be technologically important for near future applications.[3] One of our research processes led to the discovery of a series of ferromagnetic SCMs using 2:1 assemblies of Mn^{III} salen-type complexes and Ni^{II} oximate complexes with a repeat of [–Mn^{III}–ON–Ni^{II}–NO–Mn^{III}–$(O_{Ph})_2$–] that derives an $S = 3$ ground state (where –ON– and –$(O_{Ph})_2$– represent the oximate and biphanolate bridges, respectively),[4] which well demonstrated Glauber dynamics for the Ising spin reversal.[5] In this series, a family of Ni^{II} complexes possessing oximate groups were employed, because the oximate group (–NO–) acts not only as a coordinating linker but also as a good magnetic mediator ($J_{Mn-Ni}/k_B \approx -20$ K via –NO–).[4] Meanwhile, imidazolate-bridged transition-metal complexes have also been sprightly studied from the magnetochemical point of view.[6] Despite its unique potential as a coordinating linker/magnetic mediator, to our knowledge, metalloligands with the imidazolate moiety have rarely been exploited for heteronuclear systems up to the present time.[6a–6f] Hence in order to extend the range of available coordination-acceptor building units and magnetic exchange study toward the design of new magnetic materials, we have recently been exploring the development of imidazolate-bridged heteronuclear compounds consisting in a systematic combination with Mn^{III} salen complexes. Here, we report two kinds of imidazolate-bridged Mn^{III}–Fe^{III} compounds obtained employing [Fe^{III}{tren(2-fim)$_3$}] (tren(2-Hfim)$_3$ = tris{2-[(imidazole-2-yl)methylideneamino]ethyl}amine) that has three tripodally arranged imidazolate moieties: [Mn^{III}(5-MeOsalen)(H_2O)Fe^{III}{tren(2-fim)$_3$}](BPh_4)$_{0.5}$(ClO_4)$_{0.5}$·H_2O·3MeCN (**1**) and [Mn^{III}(saltmen)Fe^{III}{tren(2-fim)$_3$}](ClO_4)·4MeCN (**2**) (5-MeOsalen^{2-} = *N*,*N*′-ethylenebis(5-methoxysalicylideneiminate), saltmen^{2-} = *N*,*N*′-(1,1,2,2-tetramethylethylene)bis(salicylideneiminate)). The former is a dinuclear complex and the latter is a one-dimensional (1D) zigzag chain with the same Mn/Fe 1:1 formulation ratio, and both compounds bear a ferromagnetic exchange coupling between Mn^{III} and low-spin Fe^{III} centers mediating the imidazolate path.

Iron complexes with tren(2-Hfim)$_3$ and their derivatives have been well-studied previously.[7] Depending on the protonation of imidazole moieties, several complexes can be obtained with either Fe^{II} or Fe^{III} oxidation states, in which the Fe^{III} complex with a completely-deprotonated anionic ligand (i.e., tren(2-fim)$_3$) stabilizes the low-spin state with $S = 1/2$.[7] While energetic investigations on such imidazolate-containing molecules have been done previously, only one instance was available concerning the hetero-metal coordination-assembly using [Fe^{III}{tren(2-fim)$_3$}] as a two-dimensional (2D) network structure, [Fe^{III}{tren(2-fim)$_3$}]$_2$[Mn^{II}(hfac)$_2$]$_3$ (hfac = 1,1,1,5,5,5-hexafluoroacetylacetonate).[8]

The assembly reactions of [Mn^{III}(5-MeOsalen)(H_2O)](ClO_4) or [Mn^{III}(saltmen)(H_2O)](ClO_4) with [Fe^{III}{tren(2-fim)$_3$}] in a 1:1 molar ratio were carried out in acetonitrile. By using [Mn^{III}(5-MeOsalen)(H_2O)](ClO_4) with added $NaBPh_4$, a 1:1 discrete dinuclear form of **1** was selectively isolated.[9] On the other hand, a similar reaction with [Mn^{III}(saltmen)(H_2O)]-(ClO_4) led to a selective production of 1:1 1D chain of **2**.[10] The final structural arrangement of assembly compounds is thus strongly dependent on the coordination ability (and ligand selectivity) on the Mn^{III} complexes used and the packing effect tuned by the employed salen ligands and counter ions. Three imidazolate moieties on [Fe^{III}{tren(2-fim)$_3$}] (i.e., completely-deprotonated form) stabilize a neutral form of the complex even in solution, which show a great tendency to coordinate bare axial sites of Mn^{III} salen complexes as seen in the present Mn^{III}–Fe^{III} complexes of **1** and **2**.

The perspective drawings of **1** and **2** with atom-labeling schemes are depicted in Figures 1 and 2a, respectively (CCDC-716931 for **1** and CCDC-716930 for **2**. These data can be obtained free of charge from the Cambridge Crystallographic

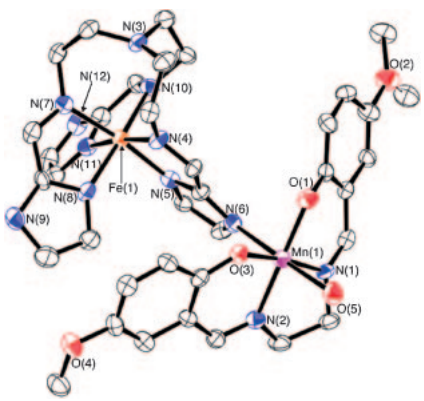

Figure 1. ORTEP drawing of the cationic moiety of **1** (30% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity.

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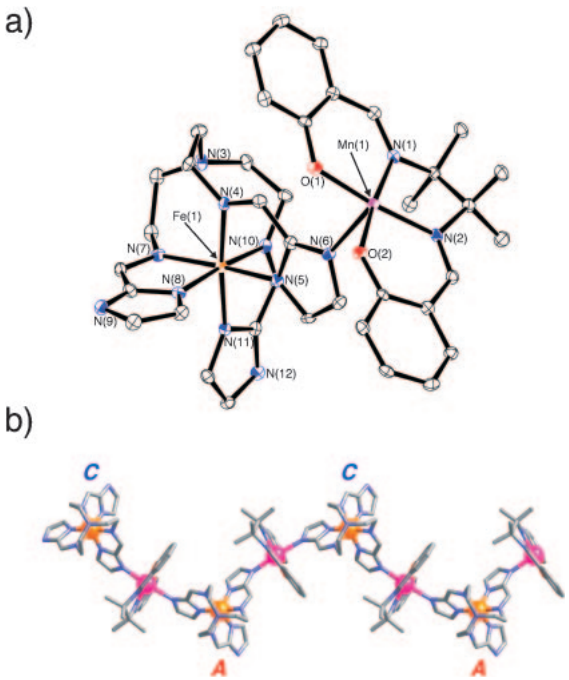

Figure 2. ORTEP drawing of the cationic asymmetric unit of **2** (a) (30% probability ellipsoid) and its chain feature (b). Hydrogen atoms are omitted for clarity.

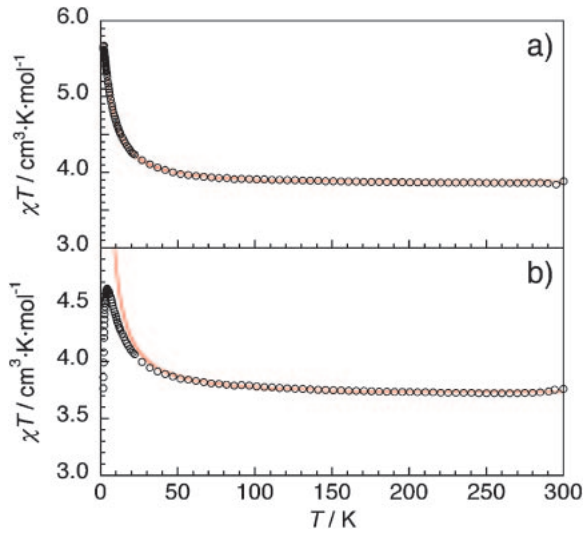

Figure 3. Temperature dependence of the χT product of **1** (a) and **2** (b). Solid red lines represent best-fit curves due to simulation using respective models (see text).

Data Centre via www.ccdc.cam.ac.uk/data_request/cif). Compound **1** consists of a monocationic dinuclear unit and two types of counter anions (B atom of tetraphenyl borate and Cl atom of perchlorate have inversion centers with an occupancy factor of 0.5, so half of the group was determined as unique atoms).[11] The area around the Mn^{III} ion assumes an elongated tetragonal geometry, where the equatorial coordination sites are occupied by an N_2O_2 donor set of 5-MeOsalen^{2-} (equatorial average bond distances are $\langle$Mn–N$\rangle = 2.005$ Å and $\langle$Mn–O$\rangle =$ 1.900 Å). The two apical positions are occupied by a deprotonated imidazolate nitrogen atom of [Fe^{III}{tren(2-fim)$_3$}] and the oxygen atom of water. The axial bond distances [Mn(1)–N(6) 2.324(6) and Mn(1)–O(5) 2.217(6) Å] are much longer than the equatorial bond distances owing to Jahn–Teller distortion. Thus, only one of three deprotonated imidazolate moieties of [Fe^{III}{tren(2-fim)$_3$}] is used for bonding with the Mn^{III} unit, consequently yielding a discrete form. The cationic unit, [Mn^{III}(5-MeOsalen)(H_2O)Fe^{III}{tren(2-fim)$_3$}]$^+$, self assembles by making a hydrogen-bonding 2D network with contacts between the water molecule coordinating on the Mn^{III} ion and the non-coordinating two imidazolate nitrogen atoms of neighboring [Fe^{III}{tren(2-fim)$_3$}] (Figure S1) (the counter anions, BPh_4^- and ClO_4^-, are located between these hydrogen-bonded sheets). Note that the clockwise (C) and anticlockwise (A) enantiomers of [Fe^{III}{tren(2-fim)$_3$}] induced by the screw coordination arrangement of the achiral tripod ligand around the Fe^{III} ion coexist as a racemic form in the crystal (respective enantiomers make 1D arrangements of ···C···C···C··· and ···A···A···A··· along the *b* axis; see Figure S1).

Compound **2** forms a cationic 1D zigzag chain with a repeat of [–Mn^{III}–im–Fe^{III}–im–] (Figure 2b).[11] Thus, two of three deprotonated imidazolate groups of [Fe^{III}{tren(2-fim)$_3$}] are used to bond with Mn^{III} units. Similar to **1**, the Mn^{III} ion takes an elongated tetragonal geometry with the Jahn–Teller distortion, where the equatorial coordination sites are occupied by an N_2O_2 donor set of saltmen^{2-} (equatorial average bond distances are $\langle$Mn–N$\rangle = 1.993$ Å and $\langle$Mn–O$\rangle = 1.890$ Å) and the apical sites are occupied by two different deprotonated imidazolate nitrogen atoms [N(6) and N(12)*] of [Fe^{III}{tren(2-fim)$_3$}] with bond lengths and angles of Mn(1)–N(6) = 2.301(3) Å; Mn(1)–N(12)* = 2.431(3) Å; and ∠N(6)–Mn(1)–N(12)* = 170.2(2)°, respectively. Angles of Fe(1)–Mn(1)–Fe(1)$^{\#\#}$ = 148.112(17)° and Mn(1)–Fe(1)–Mn(1)$^{\#}$ = 113.914(15)° ($^{\#}$ and $^{\#\#}$ denote the symmetry operation of $x + 1/2 - 1$, $-y + 1/2$, $z + 1/2 - 1$ and $x + 1/2$, $-y + 1/2$, $z + 1/2$, respectively) through the bridge of imidazolate is largely bent, forming a zigzag chain motif. The C and A enantiomers of [Fe^{III}{tren(2-fim)$_3$}] appear alternately in a chain (Figure 2b).

Static magnetic measurements were performed on hand-collected ground crystals of **1** and **2** in the temperature range of 1.8–300 K in a 1 kOe dc field. The χT value of **1** at 300 K is 3.86 cm^3 K mol^{-1}, which is larger than the predicted spin-only value 3.38 cm^3 K mol^{-1} for a set of $S = 2$ and $S = 1/2$ assuming an average g value of 2.00, then monotonically increases with decreasing temperature, and finally reaches a maximum of 5.66 cm^3 K mol^{-1} at 1.8 K (Figure 3a). The continuous increase of χT over the entire temperature region indicates the domination of intramolecular ferromagnetic coupling between Mn^{III} and Fe^{III} centers via the imidazolate linkage. Indeed, the Weiss constant obtained from a linear fit of $1/\chi$ over the entire temperature range measured is $\theta = +1.7$ K with Curie constant $C = 3.84$ cm^3 K mol^{-1}. Furthermore, the maximum χT value (5.66 cm^3 K mol^{-1}) at 1.8 K is much larger than the value of 4.38 cm^3 K mol^{-1} with $g = 2.00$ expected for the spin ground state $S_T = 5/2$, possibly suggesting the presence of intermolecular ferromagnetic interactions. This χT behavior was simulated by employing the Heisenberg–Dirac–Van Vleck hetero-dimer model with the spin system (S_{Mn}, $S_{Fe} = 2$, $1/2$) taking into account the intermolecular

magnetic interaction zJ' in the frame of the mean-field approximation [$\mathcal{H} = \mathcal{H}_{HDVV} + \mathcal{H}_{MFA}$, where $\mathcal{H}_{HDVV} = -2J_{Mn-Fe}\vec{S}_{Mn}\cdot\vec{S}_{Fe}$ and $\mathcal{H}_{MFA} = -zJ'S_T\langle S_T\rangle$]. The adequate parameter set obtained by a satisfactory fit is; $J_{Mn-Fe}/k_B = +2.24(2)$ K, $zJ'/k_B = +0.023(4)$ K, $g_{Mn} = 2.00(2)$, $g_{Fe} = 2.99(2)$, and $N\alpha = 120 \times 10^{-6}$ cm^3 mol^{-1} (fix; $N\alpha$ = temperature-independent paramagnetism).[12]

On the other hand, the χT value of **2** at 300 K is 3.76 cm^3 K mol^{-1}, which is larger than the predicted spin-only value (3.38 cm^3 K mol^{-1}, $g_{Mn} = g_{Fe} = 2.00$), then gradually increases with decreasing temperature, and reaches a maximum of 4.64 cm^3 K mol^{-1} at ca. 4 K, clearly indicating the existence of an intrachain ferromagnetic interaction between Mn^{III} and Fe^{III} ions through the imidazolate bridge, and finally below this temperature, the χT decreases gradually to 3.76 cm^3 K mol^{-1} at 1.8 K mainly due to the finite chain effect (Figure 3b). The ferromagnetic coupling is supported by the presence of positive Weiss constant of $\theta = +1.9$ K obtained from a linear fit of $1/\chi$ at temperatures above 6 K ($C = 3.70$ cm^3 K mol^{-1}). The intrachain magnetic coupling, J, was evaluated by fitting with an alternating chain model established by Drillon et al. ($\mathcal{H} = -2J_{Mn-Fe}\sum_{i-1}^{2n}\vec{S}_i\cdot\vec{S}_{i+1}$ with $S_i = S_{Mn} = 2$ and $S_{i+1} = S_{Fe} = 1/2$).[13] The adequate parameter set obtained from the fit above 50 K is; $J_{Mn-Fe}/k_B = +1.20(15)$ K, $g_{Mn} = 1.99(15)$, $g_{Fe} = 2.71(80)$, and $N\alpha = 120 \times 10^{-6}$ cm^3 mol^{-1} (fix).[12] The J_{Mn-Fe} value of **2** is approximately twice of that of **1**, but seems to be the same range. The ac susceptibility measurements prove the quasi-isotropic paramagnetic behavior at least above 1.8 K for both **1** and **2**.

In conclusion, we demonstrated here the design of imidazolate-bridged Mn^{III}–Fe^{III} assemblies by displaying the first discrete and 1D zigzag chain compounds and the existence of ferromagnetic coupling between these magnetic centers through the imidazolate bridge ($J_{Mn-Fe}/k_B = +1$–$+3$ K). The imidazolate-bridged heterometallic systems would be a good candidate especially for superparamagnetic materials such as SCMs or anisotropic nanowire quantum systems;[14] however, for which the linear arrangement of the magnetic easy-axis on individual magnetic center could be preferred.

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Supporting Information

Experimental details and packing figure of **1** (Figure S1). These materials are available free of charge on the web at: http://www.csj.jp/journals/bcsj/.

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9 For **1**: Yield 54%. Anal. (%): $C_{55}H_{65}B_{0.5}Cl_{0.5}FeMnN_{15}O_8$: C, 55.14; H, 5.47; N, 17.54. Found: C, 54.68; H, 5.35; N, 17.53. IR(KBr, cm^{-1}): $\nu(ClO_4) = 1100$, $\nu(C{=}N) = 1616$.

10 For **2**: Yield 35%. Anal. (%): $C_{46}H_{55}ClFeMnN_{16}O_6$: C, 51.43; H, 5.16; N, 20.86. Found: C, 51.11; H, 5.28; N, 20.73. IR(KBr, cm^{-1}): $\nu(ClO_4) = 1103$, $\nu(C{=}N) = 1633$.

11 A single crystals of **1** and **2** coated with Nujol in the mother liquid were mounted on nylon loops and immediately cooled at 103(1) K in the nitrogen cold stream. Measurements were conducted on a Rigaku CCD diffractometer (Saturn70) with graphite-monochromated Mo Kα radiation ($\lambda = 0.71070$ Å). The crystal dimensions were $0.60 \times 0.14 \times 0.07$ mm^3 for **1**, $0.18 \times 0.10 \times 0.01$ mm^3 for **2**. Crystal data for **1**: $C_{51}H_{58.5}B_{0.5}Cl_{0.5}FeMnN_{13.5}O_{8.5}$, fw: 1130.53, monoclinic $P2/a$ (#13), $T = 103(1)$ K, $a = 19.411(11)$ Å, $b = 12.024(7)$ Å, $c = 25.613(15)$ Å, $\beta = 92.539(10)°$, $V = 5972(6)$ Å^3, $Z = 4$, $D_{calcd} = 1.257$ g cm^{-3}, $F_{000} = 2356$, $\mu(\text{Mo K}\alpha) = 5.366$ cm^{-1}, final $R_1 = 0.1014$ ($I > 2.00\sigma(I)$), $R_1 = 0.1663$ (all data), $wR_2 = 0.2697$ (all data), GOF = 1.001, $\Delta\rho_{max} = 1.24$ e$^-$/Å^3, $\Delta\rho_{min} = -0.89$ e$^-$/Å^3. Crystal data for **2**: $C_{46}H_{55}ClFeMnN_{16}O_6$, fw: 1074.28, monoclinic $C2/c$ (#15), $T = 103(1)$ K, $a = 25.868(12)$ Å, $b = 27.268(11)$ Å, $c = 18.400(9)$ Å, $\beta = 128.401(6)°$, $V = 10171(8)$ Å^3, $Z = 8$, $D_{calcd} = 1.403$ g cm^{-3}, $F_{000} = 4472$, $\mu(\text{Mo K}\alpha) = 6.493$ cm^{-1}, final $R_1 = 0.0681$ ($I > 2.00\sigma(I)$), $R_1 = 0.1032$ (all data), $wR_2 = 0.1711$ (all data), GOF = 1.210, $\Delta\rho_{max} = 1.17$ e$^-$/Å^3, $\Delta\rho_{min} = -0.64$ e$^-$/Å^3.

12 The g_{Fe} values estimated for **1** and **2** seem to be a little too large, although Fe^{III} complexes in the $^2T_{2g}$ state commonly have large g_{Fe} values often being ca. 2.6, which is currently unclear; further investigations are needed.

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