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New Approach for Designing Single-Chain Magnets: Organization of Chains via Hydrogen Bonding between Nucleobases

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Supporting Information

ABSTRACT: Two one-dimensional (1D) manganese complexes, $[Mn_2(naphtmen)_2(L)](ClO_4)\cdot 2Et_2O\cdot 2MeOH\cdot H_2O$ (**1**) and $[Mn_2(naphtmen)_2(HL)](ClO_4)_2\cdot MeOH$ (**2**), were synthesized by using a bridging ligand with a nucleobase moiety, 6-amino-9-β-carboxyethylpurine, and a salen-type manganese(III) dinuclear complex, $[Mn_2(naphtmen)_2(H_2O)_2](ClO_4)_2$ (naphtmen^{2-} = *N*,*N*′-(1,1,2,2-tetramethylethylene)bis(naphthylideneiminato) dianion). In **1** and **2**, the carboxylate-bridged Mn^{III} dinuclear units are alternately linked by two kinds of weak Mn···O interactions into 1D chains. As a result, canted antiferromagnetic and ferromagnetic interactions are alternately present along the chains, leading to a 1D chain with non-cancellation of anisotropic spins. Since the chains connected via H-bonds between nucleobase moieties are magnetically isolated, both **1** and **2** act as single-chain magnets (SCMs). More importantly, this result shows the smaller canting angles hinder long-range ordering in favor of SCM dynamics.

Single-molecule magnets (SMMs) and single-chain magnets (SCMs) exhibit quantum magnetism and magnetic relaxation phenomena in contrast to bulk magnets.[1] To construct SMMs, magnetically isolated molecules must have large spin ground states and uniaxial magnetic anisotropy.[2] In general, SMMs are prepared by forming discrete clusters of paramagnetic centers with high magnetic anisotropy via ligands that can mediate the magnetism, causing a higher spin ground state. On the other hand, SCMs are composed of one-dimensional (1D) chain complexes with magnetic coupling along the chain and non-cancellation of the uniaxial anisotropic spins. The chains should be as magnetically isolated as possible, meaning that the magnetic interchain interactions must be very weak compared to intrachain coupling in order to avoid the stabilization of 3D magnetic ordering.[3] Thus, large counterions and bulky molecules have been used to prepare SCMs.[4] In this paper, we propose a new synthetic approach for preparing SCMs, in which H-bonded nucleobase groups are used to isolate/arrange 1D SCMs in a crystal. In this study, we used 6-amino-9-β-carboxyethylpurine (HL) as a bridging ligand and exploited the H-bonding ability of adenine group as the nucleobase moiety to link the chains.[5] The salen-type Mn^{III} complex $[Mn_2(naphtmen)_2(H_2O)_2](ClO_4)_2$ (naphtmen^{2-} = *N*,*N*′-(1,1,2,2-tetramethylethylene)bisnaphthylideneiminato dianion), which has a large magnetic anistropy, was used as a building block.[6]

The 1D Mn complex $[Mn_2(naphtmen)_2(L)](ClO_4)\cdot 2Et_2O\cdot 2MeOH\cdot H_2O$ (**1**) was synthesized by reacting HL and triethylamine with the Mn^{III} complex $[Mn_2(naphtmen)_2(H_2O)_2](ClO_4)_2$ (see SI). $[Mn_2(naphtmen)_2(HL)](ClO_4)_2\cdot MeOH$ (**2**) was obtained by a similar reaction without triethylamine; namely, the adenine group of **2** was protonated. From single-crystal X-ray crystallography, both complexes crystallized in the triclinic space group $P\bar{1}$ (see SI). In their asymmetric units, two crystallographically independent Mn(naphtmen) units, with the naphtmen ligands in a quasi-plane chelate mode, are bridged by a carboxylate group in a *syn*−*anti* mode (Figures S1, S2). As shown in Figure 1, the resulting carboxylate-bridged Mn^{III} dinuclear units are alternately linked by two types of weak Mn···O_{Ph} coordination interactions, which form out-of-plane dimers often observed in salen-type Mn^{III} SMMs.[7] As a result, a 1D chain structure with a [···Mn−(CO_2)−Mn···$(O_{Ph})_2$···] repeat was formed along the (011) crystallographic axis in **1** and the *c* axis in **2**. Both compounds have H-bonds between adenine moieties of adjacent chains (Figure 1, right). In **1**, the adenine groups interact with the adenine groups of neighboring chain through the proton of the amine group (N9) and the 1-position nitrogen atom (N5*). In **2**, however, adenine groups are protonated at the 1-position nitrogen atom (N5). Therefore, H-bonds form between a proton of amine group (N9) and the 7-position nitrogen atom (N8*). These H-bonds differ from those of the complementary base pair in DNA and link the chains to form 2D layers in the *bc* plane for **1** and the (220) crystallographic plane for **2** (Figure S3). The counteranions and/or the disordered solvent molecules fill the space between the 2D layers. The closest atomic distance between the paramagnetic metal ions of adjacent chains is 12.642(3) Å for **1** and 10.905(1) Å for **2**. As a result, the H-bonds and solvent molecules effectively separate the chains, in contrast to reported analogues with no H-bonds and solvent molecules between magnetic chains.[8] H-bonding between the chains causes a

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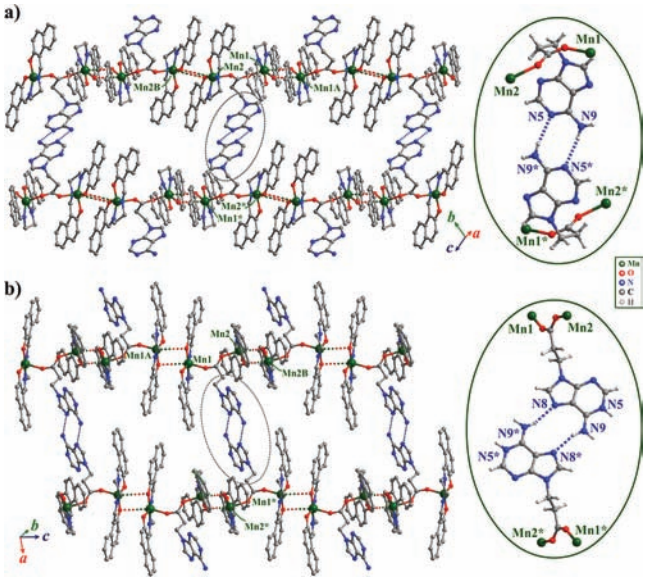

Figure 1. 1D chains of (a) **1** and (b) **2**. H atoms, solvent molecules, ClO_4^- anions, and the methyl groups of the naphtmen units have been omitted for clarity. Details of H-bonding between the adenine moieties are shown on the right. Symmetry operations: for **1**, (A) $-x+2, -y, -z$; (B) $-x+2, -y+1, -z+1$; (*) $-x+2, -y, -z+1$; for **2**, (A) $-x, -y+1, -z$; (B) $-x, -y+1, -z+1$; (*) $-x+2, -y, -z+1$.

dramatic difference in the magnetic properties of the analogues and **1** and **2**.

Magnetic measurements were performed on ground polycrystalline samples of **1** and **2** in a dc field of 1 kOe. As shown in Figure 2a, the χT values at 300 K were 5.96

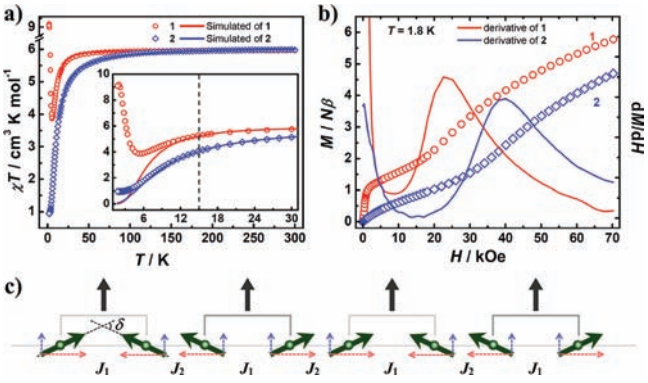

Figure 2. (a) Variable-temperature dc magnetic susceptibility data for **1** (red) and **2** (blue) collected in an applied field of 1 kOe. The solid line is a fit of the data, as described in the text. (b) Field-dependent magnetizations and its derivative of **1** (red) and **2** (blue) at 1.8 K. (c) Diagram of the spin canting in **1** and **2**. The green arrows represent the spins of the Mn^{III} ions, which could be divided into uncompensated and compensated components shown as blue and red dashed arrows, respectively. The resulting net magnetic moments (black arrows) in the AF dimers are parallel to each other in a 1D arrangement.

$cm^3 \cdot mol^{-1} \cdot K$ for **1** and 5.98 $cm^3 \cdot mol^{-1} \cdot K$ for **2**, close to the value expected for two uncorrelated Mn^{III} ions (6.00 $cm^3 \cdot mol^{-1} \cdot K$). The χT values gradually decreased with decreasing temperature, reaching 3.87 $cm^3 \cdot mol^{-1} \cdot K$ at 5.4 K for **1** and 0.98 $cm^3 \cdot mol^{-1} \cdot K$ at 3.0 K for **2**. When the temperature was lowered further, the χT value for **1** gradually increased, whereas that for **2** scarcely changed. As shown in Figure 1, two different intrachain magnetic bridges are alternately present along the chain:[9] *syn–anti* carboxylate bridges (labeled as J_1), which usually pass antiferromagnetic (AF) interactions, and phenolate bridges (labeled as J_2), which usually pass ferromagnetic (F) interactions due to accidental orthogonality of magnetic orbitals.[7] The magnetic susceptibility data in the higher temperature region suggest that J_1 is dominant in both **1** and **2**.

To clarify the magnetic interactions, the data above 14 K were analyzed by using a Heisenberg dimer model with $S = 2$ and the zero-field splitting term (D) for each Mn^{III} ion (spin Hamiltonian $\mathbf{H} = -2J_1S_1S_2 + 2D[S_z^2 - S(S+1)/3]$, $S_1 = S_2 = 2$). The analysis afforded $g = 1.99$, $J_1 = -0.97$ K, $D = -3.21$ K, and the residual factor $R = \sum(\chi_{obs}T - \chi_{cal}T)^2/\sum(\chi_{obs}T)^2 = 2.4 \times 10^{-5}$ for **1** and $g = 2.01$, $J_1 = -1.48$ K, $D = -1.46$ K, and $R = 3.2 \times 10^{-6}$ for **2**. The D values are consistent with the typical value for Mn^{III} salen analogues and the presence of Jahn–Teller distortion in these compounds.[6,10] The negative J_1 values further confirm that AF interactions through the single *syn–anti* carboxylate bridges are dominant and are consistent with the distinct inflection points, at which the fields (H_{ex} = 23 kOe for **1** and 40 kOe for **2**, Figure 2b) overwhelm the AF interactions. The inflection points make it possible to roughly estimate the AF interactions using $2|zJ_1|S^2 = gS\mu_B H_{ex}$ with $z = 1$ and $g = 2.0$: $|J_1| = 0.77$ K for **1** and 1.32 K for **2**, similar to the values estimated from simulations of χT.

No inversion center exists between Mn1 and Mn2 ions linked by the *syn–anti* carboxylate bridges. In addition, their Jahn–Teller axes are not parallel to each other but form an angle θ of 46.1(1)° in **1** and 23.6(1)° in **2**, estimated from the structure in Figure S4. Thus, a canted arrangement of spins is formed due to the antisymmetric magnetic exchange interactions in the carboxylate-bridged dinuclear units, leading to small net magnetic moments.[11] It should be pointed out that the canting angle δ in Figure 2c is smaller than θ because the AF interactions cause the spin vectors to align antiparallel; it was estimated from J_1, D, and θ to be 29° for **1** and 7.7° for **2**.[12] As shown in Figure 2c, the resulting small net magnetic moments are correlated ferromagnetically with $J_2 > 0$ along the chain. Thus, the values of χT for **1** increased at lower temperatures, although they remained constant for **2** due to a very small net magnetic moment compared to that for **1** (vide infra). These observations satisfy one of the requirements for SCMs: 1D chains with magnetic coupling along the chain and non-cancellation of the anisotropic spins.

Ac magnetic susceptibility measurements on powder samples of **1** and **2** were performed in the temperature range of 1.8–4.0 K (Figure 3). Both in-phase (χ') and out-of-phase (χ'') components were dependent on the frequency, and their peak maxima shifted to lower temperatures as the AC frequency was lowered, indicating slow relaxation of the magnetization of **1** and **2**, characteristic of SCMs. The data from 1.8 to 2.8 K in a zero dc field were fitted by using a generalized Debye model[13] (Figure 4a,b), affording the parameter α in the range of 0.04–0.14 for **1** and 0.12–0.28 for **2** (see SI). Thus, their relaxation times $\tau(T)$ have relatively narrow distributions. Similar complexes with an identical bridging motif composed of Mn^{III} salen complexes and carboxylate groups, such as cinnamate, phenylacetate, and benzoate, exhibit no SCM behavior because of the presence of AF long-range ordering.[8] H-bonding between nucleobase

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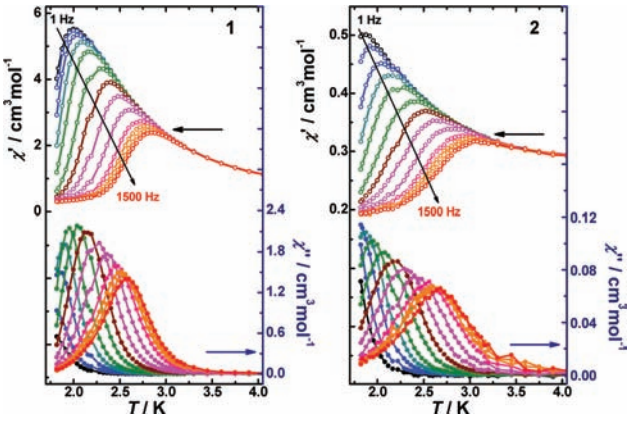

Figure 3. Temperature-dependent ac magnetic susceptibility of **1** (left) and **2** (right) with an oscillation of 3 Oe in zero dc magnetic field.

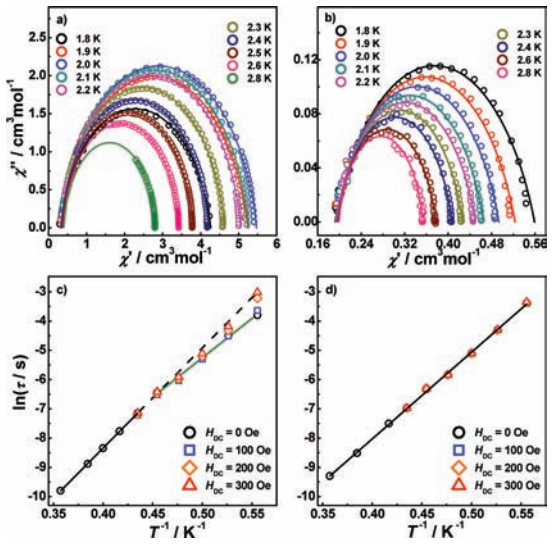

Figure 4. Cole−Cole plots of (a) **1** and (b) **2**. The open circles and the solid lines correspond to the experimental data and curves simulated using best fitting parameters, respectively (see SI). Arrhenius plots for (c) **1** and (d) **2**.

moieties of neighboring chains is crucial for SCM behavior in **1** and **2**.

Although the chains of **1** are well-organized with a relatively long interchain distance (>12 Å), an anomaly in the χ'' vs T behavior of **1** at low temperatures (Figure 3) was observed. The temperature-dependent behaviors of $\tau(T)$ of **1** and **2** in the absence of a magnetic field were a little different, although both of them followed the Arrhenius law: $\tau(T) = \tau_0 \exp(\Delta/kT)$, where τ_0 is a prefactor and Δ is the activation barrier. For **1**, fitting the data above and below 2.2 K afforded Δ = 34 and 27 K, respectively (solid black and green lines in Figure 4c), likely caused by the finite-size effect of SCMs.[1] However, by applying a small dc field (ca. 300 Oe), $\tau(T)$ increased (Figure 5a) and was located on an extension of the fitted line above 2.2 K at zero field (dashed black line in Figure 4c), suggesting an AF ordered phase in **1**. The AF ordered phase was further confirmed on the basis of the derivatives of field-dependent magnetization (Figure S5), field cooling curves (Figure S6), and $\ln(\chi T)$ vs T^{-1} plots (Figure 5b) in applied dc magnetic fields of 0−400 Oe. In this range, the maxima of $\ln(\chi T)$ shifted to lower temperatures and nearly vanished in an applied field of

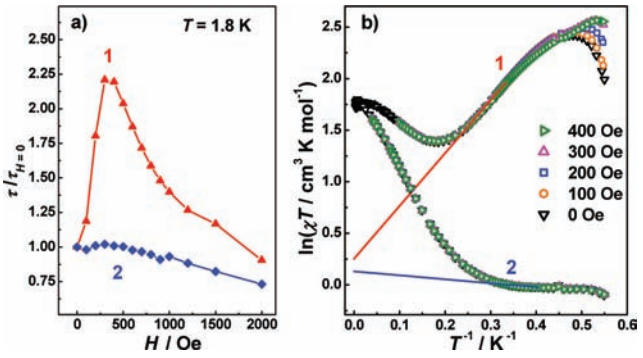

Figure 5. (a) Field-dependent relaxation times (normalized at zero field) of **1** and **2** at 1.8 K. (b) $\ln(\chi T)$ vs T^{-1} plots for **1** and **2** in applied dc magnetic fields of 0−400 Oe. The solid lines were fitted to the linear portion of the data in a zero field for **1** (red) and **2** (blue).

400 Oe, proving the coexistence of slow relaxation of the magnetization and an AF phase in **1** below 2.2 K.[3] On the other hand, in the case of **2**, no AF ordered state was observed above 1.8 K, and the values of $\tau(T)$ in the temperature range of 1.8−2.8 K followed the Arrhenius law with Δ = 30 K (Figure 4d), meaning that **2** is a normal SCM. As mentioned before, the chain packing in **1** and **2** is quite similar, and the interchain distance in **1** is longer than that in **2**, which implies that the interchain H bonds are not the main reason for the higher ordering temperature for **1** than for **2** (vide infra).

As shown in Figure 2c, the 1D chains of **1** and **2** at low temperature can be simplified as non-regular chains with alternating J_1 and J_2. It has been proposed that $\Delta = 4(|J_1| \cos(\delta) + J_2)S^2 + |D|S^2$ for single spin-flip processes when the amplitudes of J_1 and J_2 are similar.[14] By using the obtained values of J_1, D, and δ and J_2 = 0.2 K, we calculated Δ = 30 K for **1** and 32 K for **2**, consistent with the experimental values of 34 and 30 K for **1** and **2**, respectively.

In the 1D uniform F uniaxial anisotropic chain, the correlation length ξ at low temperatures increased exponentially with decreasing T, leading to an exponential increase in χT values: $\chi T \propto \exp(\Delta_\xi/T)$. Thus, the slope Δ_ξ obtained from linear analysis of $\ln(\chi T)$ vs T^{-1} is directly related to the exchange contribution for an SCM.[1] However, it has been shown that this linear analysis is not directly related to the exchange contribution for a canted AF SCM.[15] Indeed, the value of Δ_ξ obtained by fitting the $\ln(\chi T)$ vs T^{-1} plot for **1** in a zero field in the linear region was 5.0 K, whereas the exchange contribution for **1** estimated from $(\Delta - |D|S^2)/2$ was 10.6 K.[16] In addition, the values of χT for **2** did not increase with a decrease in T, leading to a negative slope (−0.38 K) in the linear region of the $\ln(\chi T)$ vs T^{-1} plot (Figure 5b); this behavior is similar to that observed for SCMs of AF chains.[17]

As shown in Figure 2c, the spin vector S can be decomposed into two components: an uncompensated part ($S \sin(\delta/2)$) and a compensated part ($S \cos(\delta/2)$), which are perpendicular and parallel to the chain, respectively, for $\delta < 90°$. As T was lowered, the 1D F-interacted uncompensated component caused an increase in χT, whereas the compensated component caused χT to decrease monotonically to zero. The experimentally observed χT behavior for a powder sample is due to this competition, and it decreases monotonically with a decrease in T if δ is too small to produce a large enough uncompensated component, which is the case for **2**. On the other hand, $\ln(\xi)$ along the chain is proportional to $|J_1| \cos(\delta)$ +

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J_2 in the present case.[1b,14,15] For given J_1 and J_2, smaller δ leads to a steeper increase in ξ with a decrease in T. This analysis roughly shows that the relation between χT and ξ is not straightforward in the present case, and the analysis on χT will seriously underestimate the exchange contribution in the case of small δ.

On the other hand, in theory, the deviation of χT and ξ is advantageous for the preparation of canted AF SCMs. That is, the smaller δ hinders 3D ordering in favor of SCM dynamics. It is well known that chains are actually packed in a 3D crystal, and an interchain interaction J'' cannot be eliminated completely because dipolar interactions must be considered.[1c] For a given J'', the 3D-ordering phase transition temperature T_{3D} is higher the steeper the divergence of χ_{1D} with T.[18] In the case of a canted AF chain with a small δ, the divergence of χ_{1D} with T falls behind that of ξ/T, and the smaller δ is, the more serious lag is. Indeed, the quite similar SCM behaviors of **1** and **2** indicate that they have almost the same divergence of ξ/T with T. However, the larger δ in **1** makes the divergence of χ_{1D} much steeper than that of **2**, leading to a higher phase transition temperature for **1**, even though the interchain distance is greater in **1** than in **2**. This explains why an AF ordered state of SCM was observed for **1** but not for **2** at $T < 2.2$ K.

In conclusion, two Mn^{III} chain complexes with alternating canted AF and F interactions were obtained by linking salen-type Mn^{III} out-of-plane dimers with a bridging carboxylate ligand including an adenine moiety. The good organization of chains via H-bonds of adenine moieties between adjacent chains allowed them to behave as SCMs. More importantly, for the first time, we showed that a smaller canting angle hindered 3D ordering in favor of SCM dynamics. Thus, by controlling the structure via H-bonds between nucleobase groups and the intrachain spin arrangement via canting modes, we designed a new SCM system, although similar systems are 3D magnets.[8] The relationship between the size of the canting angle and the observation of SCM behavior is under investigation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic files in CIF format and additional structural and magnetical data for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(16) In Ising-like canted AF SCM, the equation $\Delta = 2\Delta_\xi + \Delta_A$ is still valid for single spin-flips in the infinite chain limit, where Δ_A is the single ion anisotropy and equals $|D|S^2$ in the present case.

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