A canted antiferromagnetic ordered phase of cyanido-bridged Mn\textsuperscript{III}–Re\textsuperscript{IV} single-chain magnets

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A new cyanido-bridged Re\textsuperscript{IV}–Mn\textsuperscript{III} heterometallic 1D system, [Mn\textsuperscript{III}(5-Me-saltmen)][Re\textsuperscript{IV}Cl\textsubscript{4}(CN)\textsubscript{2}]\textsubscript{3}CH\textsubscript{3}CN (I), was designed and structurally characterized. Interchain interactions stabilize a canted antiferromagnetic ordered state below 6.2 K that does not prevent slow relaxation of the magnetization reminiscent of the single-chain magnet properties of the individual chains.

Fig. 1 View of the crystal structure of the chain in I. Orange, purple, green, red, blue and black ellipsoids (shown at 30% probability) represent the Re, Mn, Cl, O, N and C atoms respectively. Solvent molecules and hydrogen atoms have been omitted for clarity.

For the first time in 2001, slow relaxation of the magnetization was reported in a one-dimensional (1D) Ising-type system, although this dynamic property was predicted almost 40 years earlier by R. J. Glauber.\textsuperscript{2} Since then, many other examples, called Single-Chain Magnets (SCMs),\textsuperscript{3,4} have been discovered.\textsuperscript{3,4} In a mere ten years, the design and study of these molecule-based magnets has become an important research field in coordination chemistry and molecular magnetism. Unlike Single-Molecule Magnets (SMMs), for which the slow dynamics are induced only by the combination of magnetic anisotropy and a high spin ground state, the magnet behavior observed in SCMs is also due to intrachain interactions, which promote the development of large magnetic domains along the chain.\textsuperscript{6}

In order to synthesize new SCM systems, a rational approach requires the use of preformed building units with appropriate geometry, coordination abilities and magnetic characteristics.\textsuperscript{6} Recently, a \textit{trans}-dicyanide Re\textsuperscript{IV} precursor, [Re\textsuperscript{IV}Cl\textsubscript{4}(CN)\textsubscript{2}]\textsuperscript{2–}, possessing a large magnetic anisotropy and an \( \mathbb{S}_1 = \mathbb{S}_0 / 2 \) spin ground state was reported.\textsuperscript{7,8} Due to the \textit{trans} positions of the \( -(CN) \) groups, this Re\textsuperscript{IV} complex favors the formation of 1D coordination architectures\textsuperscript{7–11} possessing, in many cases, SCM properties.\textsuperscript{7–9} While in these systems, [Re\textsuperscript{IV}Cl\textsubscript{4}(CN)\textsubscript{2}]\textsuperscript{2–} units were only associated with simple mononuclear paramagnetic complexes,\textsuperscript{7–11} we herein report the use of the \textit{trans}-[Re\textsuperscript{IV}Cl\textsubscript{3}(CN)]\textsuperscript{2–} anion to link dinuclear \( \mathbb{S}_1 = \mathbb{S}_0 / 4 \) Mn\textsuperscript{III}-Schiff base SMMs\textsuperscript{12} into a 1D coordination network.

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The static and dynamic magnetic properties of I were thoroughly studied using both dc and ac susceptibility techniques. The temperature dependence of the $\chi T$ product at 1000 Oe is shown in Fig. 2. At 280 K, the value of $\chi T$ is 7.9 cm$^3$ K mol$^{-1}$, in good agreement with the expected Curie constant of 7.4 cm$^3$ K mol$^{-1}$ considering $g$ factors of 2 and 1.7 for isolated Mn$^{III}$ ($S = 2$) and Re$^{IV}$ ($S = 3/2$) spin carriers. Below 280 K, $\chi T$ decreases with temperature to reach a minimum value of 5.6 cm$^3$ K mol$^{-1}$ at 39 K. Lowering the temperature further results in a sudden $\chi T$ increase up to 13.5 cm$^3$ K mol$^{-1}$ at 7.4 K followed by a final decrease down to 2.1 cm$^3$ K mol$^{-1}$ at 1.8 K.

The $\chi T$ vs. $T$ data (Fig. 2) are consistent with relatively strong Re$^{IV}$-$\cdot$Mn$^{III}$ antiferromagnetic (AF) interactions ($J$) mediated by the cyanido ligands, and weak ferromagnetic ($J'$) interactions between the Mn$^{III}$ spins through the double phenoxido bridges. Therefore the 1D network seen in I can be described as an assembly of trinuclear Mn$^{III}$–Re$^{IV}$–Mn$^{III}$ units weakly interacting ferromagnetically along the chain. The data were thus modeled using an isotropic trinuclear ($S_{Mn} = 2$, $S_{Re} = 3/2$)–Mn$^{III}$–Mn$^{III}$ Hamiltonian $H = -2J(S_{Mn} + S_{Mn})S_{Re}$ and considering the Mn$^{III}$–Mn$^{III}$ interactions, $J'$, in the frame of the mean field approximation. This approach well reproduced the experimental $\chi T$ vs. $T$ data (solid red line in Fig. 2) above 10 K, yielding the parameters: $g = 2.10(5)$, $J/k_B = -10.8(6)$ K and $zJ'/k_B = + 10.1(1)$ K. Thus, at low temperature, I can be considered as a chain of ferromagnetically coupled S$_T = 5/2$ spins. Note that the $J$ value is close to but slightly larger than that of $J/k_B = -7.8(6)$ K observed for the related compound (DMF)$_2$MnReCl$_5$(CN)$_2$. In order to examine the 1D behavior of I and the magnitude of the $J'$ intrachain interaction, the temperature dependence of the correlation length, $\xi$, was estimated from $\chi T$. As in any 1D classical system, $\xi$ is directly proportional to $\chi T$ in zero dc field. For Ising-like or anisotropic Heisenberg spins, $\chi T$ increases exponentially with lowering temperature where $\chi T \approx C_{eff} \times \exp(\Delta_c/k_B T)$ ($C_{eff}$ is the effective Curie constant and $\Delta_c$ is the energy to create a domain wall in the chain). As shown in the inset of Fig. 2, the ln($\chi T$) vs. $1/T$ plot is linear between 25 and 10 K demonstrating the magnetic 1D behavior of I and the expected presence of significant magnetic anisotropy. From these data, $\Delta_c$ is evaluated at 11.6 K and thus within the Ising limit ($DJ/k_B > 4/3$, $\Delta_c/k_B = 4J/k_B^2$), and $J'/k_B = + 0.46$ K in excellent agreement with the above mean-field estimation ($z = 2$). Below 10 K, ln($\chi T$) deviates from linearity, as expected when interchain interactions are present or when the magnetic correlation is physically limited by structural defects.

In order to probe the nature of the magnetic ground state of I, the temperature and field dependence of the magnetization and susceptibility were systematically measured below 15 K (Fig. 3 and S3–S6, ESI$^\dagger$). The $\chi$ vs. $T$ data exhibit a marked maximum below 6.2 K at low fields (~3000 Oe, Fig. S3, ESI$^\dagger$), while the $M$ vs. $H$ plots display an “S shape” variation below 6.2 K (Fig. 3 and S4–S6, ESI$^\dagger$). The magnetic ($T$, $H$) phase diagram shown in the inset of Fig. 3 was built based on the maxima of the $\chi$ vs. $T$ (Fig. S5, ESI$^\dagger$) and $dM/dH$ vs. $H$ (Fig. S5, ESI$^\dagger$) data. The topology of this ($T$, $H$) diagram accords well with a 3D AF ordered state that is stabilized below $T_C = 6.2$ K in zero dc field. Under an applied dc field, I displays a metamagnetic behavior associated with a critical field extrapolated at 0 K to be $H_C(0) \approx 2600$ Oe. From this field, the average interchain interaction was estimated to be $J_{\text{perp}}/k_B = -18$ mK through the relation $2zJ_{\text{perp}}S_T^2 = g\mu_B H_C(0)S_T$ (with $z = 4$, see Fig. S2, ESI$^\dagger$). Considering the experimental 1D correlation length shown in the inset of Fig. 3 and in Fig. S8 (ESI$^\dagger$), the theoretical $T_C$ for the quasi-1D model (with $J_{\text{perp}}/k_B = -18$ mK) was estimated as 6.15 K, in excellent agreement with the experimental value.

Interestingly, despite the unambiguous presence of a magnetic phase transition in I, slow relaxation of the magnetization is observed in the $M$ vs. $H$ data at low fields (Fig. 3 and S6, ESI$^\dagger$). Indeed, $M$ vs. $H$ hysteresis loops are systematically detected below 6.2 K (Fig. S7, ESI$^\dagger$) with coercive fields up to 2100 Oe at 180 Oe min$^{-1}$ and a remnant magnetization of $M_R = 0.19$ $\mu_B$ at 1.8 K. Compound I is thus a magnet below 6.2 K, which can only be induced by a canting of two magnetic sublattices in the ordered phase. This result is not surprising on the basis of the above structural description, as two chain orientations are present in the packing. In the canted AF phase, the equilibrium canting angle, $\alpha$, between the two magnetic sublattices is estimated as $8^\circ$ from the remnant magnetization (with $\sin(\alpha/2) = 2M_R/M_{sat}$, $M_{sat} \approx 5.3$ $\mu_B$ being the magnetization at saturation with $g = 2.12$).

The slow dynamics of the magnetization in I was studied by ac susceptibility measurements (Fig. 4 and S9–15, ESI$^\dagger$). Under zero dc field, the imaginary component ($\chi''$) of the ac susceptibility is very weak in intensity but clearly shows (1) a...
frequency-independent peak around 6.2 K expected at the paramagnetic/canted AF phase transition and (2) a strongly frequency-dependent relaxation mode below 4 K (also detected on the real part of the ac susceptibility, $\chi''$). The associated relaxation time of this latter mode was deduced from the $\chi''$ vs. $\nu$ data below 3.2 K (Fig. S10, ESIF) and was found to follow an Arrhenius law ($\tau(T) = \tau_0 \exp(A/\kappa BT)$) with $\Delta/k_B = 36.4$ K and $\tau_0 = 9 \times 10^{-10}$ s. As already reported in 3D AF ordered phases of SCMs, 14 the application of a dc field slows down the observed dynamics in $\chi$ (e.g. at 3 K, from 767 Hz at 0 Oe to 61 Hz at 2400 Oe, Fig. S11–S13, ESIF) with an optimum field around 2400 Oe, i.e. near the canted AF/paramagnetic transition line. At 2400 Oe, the relaxation time estimated from the ac data shown in Fig. 4 follows two thermally activated regimes above and below 2.6 K with $\Delta/k_B = 48.6$ K ($\tau_0 = 2.3 \times 10^{-10}$ s) and $\Delta/k_B = 36.6$ K ($\tau_0 = 2.2 \times 10^{-8}$ s) respectively. We note that $\Delta/k_B$ is almost identical to $\Delta/k_B$ observed in zero dc field for $\chi$, however an explanation for this observation is not immediately forthcoming. As expected for a SCM, the difference between these two energy barriers, 12 K, agrees well with the experimental $\Delta/k_B$ (11.6 K) and thus the intrachain interactions. On the basis of the known theory on SCMs, the anisotropy barrier, $\Delta/k_B$ was tentatively evaluated at 24.6 K from the difference between $\Delta/k_B$ and $\Delta/k_B$. Subsequently, the anisotropy parameter $D$ (defined by $H = DS_1^2$ for the trinuclear $S_1 = 5/2$ MnIII-ReIV-MnIII unit was estimated at 4.1 K ($\Delta/k_B = D(S_1^2-1/4)$) in agreement with previous related systems. 15–17

The observation of a crossover on the relaxation time is unprecedented in a 3D ordered phase of SCMs, having only been previously seen in SCMs when defects limit the growth of the 1D correlation length. 9,6 Based on the crossover temperature, $T^* = 2.6$ K, and $\Delta/k_B = 11.6$ K, the average number of chain units ($n \approx 2z_\perp \approx \exp(A/k_B T^*)$) is estimated as 87 in this compound ($L \approx 120$ nm, similar to related SCMs). 4 If one naively considers that the chains in 1 are decoupled by the applied dc field at the canted AF/paramagnetic transition line, it becomes natural to expect that the experimental dynamics of 1 at 2400 Oe would be quasi-identical to the zero dc field slow relaxation of a hypothetical isolated [(MnIII(5-Me-saltmen)][ReIVCl4(CN)2]]3+ SCM. This detailed study demonstrates that the magnet behavior of 1 finds its origin in the intrinsic slow dynamics of the 1D coordination network (i.e. single-chain magnet behavior) composing this material.

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Notes and references

† Synthesis of I: [MnIII(5-Me-saltmen)(H2O)2(ClO4)2] (0.01 mmol) and 0.01 mmol of (Bu4N)[ReIVCl4(CN)2]2DMA were separately dissolved in 2 ml of acetonitrile. The MnIII solution was poured into a tube of 1.5 cm diameter and layered with 2 ml of CH2Cl2. Over this, the ReIV solution was carefully layered to avoid fast mixing of the reactants. The tube was then sealed with Parafilm to avoid evaporation. After 2 days brown needle-shaped crystals were found at the bottom and wall of the tube. Yield: 85% on the basis of the MnIII precursor; elemental analysis calcd (%) for C52H61Cl4Mn2N9O4Re (M = 1313.98 g mol−1): C, 47.53; H, 4.68; N, 9.59; found (%) as C, 47.28; H, 4.75; N, 9.85; IR (KBr): $\tilde{v} = 2141$ (C≡N stretch), 1596 (C≡N stretch) cm−1.

‡ Crystallographic data for I: C52H61Cl4Mn2N9O4Re. monoclinic, $a = 11.5321(29)$, $b = 17.45220(50)$, $c = 14.08240(40)$ Å, $\beta = 93.2088(18)$°. $V = 2829.788(135)$ Å3, $T = 150$ K, space group $P2_1/c$ (no. 14), $Z = 2$, 12 187 reflections measured, 6435 unique ($R_B = 0.0404$), final $R_1$ and $wR_2$ (all reflections) were 0.0506 and 0.0807.

