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A One-Dimensional Coordination Polymer Assembled from a Macrocyclic Mn(III) Single-Molecule Magnet and Terephthalate

Sébastien Dhers, Rajni K. Wilson, Mathieu Rouzières, Rodolphe Clérac,* and Sally Brooker*

Herein the strategy of deliberate assembly of stable soluble macrocyclic single-molecule magnets (SMMs), using appropriately chosen linkers to bridge the axial sites, as a controlled way of forming single-chain magnets (SCMs) is tested. First, the manganese(III) macrocyclic complex, $[\text{Mn}^{\text{III}}(\text{L}^{\text{Pr}})(\text{NCS})_2]$ (**1**), of the monoanionic tetradentate equatorial-N4-donor macrocyclic $(\text{L}^{\text{Pr}})^-$ ligand (formed from [1 + 1] Schiff base condensation of 2,2'-iminobisbenzaldehyde and dipropylenetriamine) is shown to be an SMM. Then, the 1:1 reaction of SMM **1** with sodium terephthalate linkers in $\text{H}_2\text{O}/\text{DMF}$ is shown, by X-ray structure determination, to form dark red single crystals of the desired one-dimensional (1D) coordination polymer, $[\text{Mn}^{\text{III}}(\text{L}^{\text{Pr}})(\text{tpa})]_n \cdot n\text{H}_2\text{O} \cdot 0.5n\text{DMF}$ (**2**), of alternating dicationic macrocycles $[\text{Mn}^{\text{III}}(\text{L}^{\text{Pr}})]^{2+}$ (from **1**) linked by the bridging dianionic linkers $[\text{tpa}]^{2-}$. Despite having the desired structural features, magnetic measurements show that **2** is an SMM, not an SCM, as the coupling along the 1D coordination polymer is negligible (with $\Delta_{\text{eff}}/k_{\text{B}} = 13.7(5)$ K and $\tau_0 = 1.4(5) \times 10^{-7}$ s). Future attempts to use this strategy of linking macrocyclic SMMs together to access SCMs will clearly require the use of linkers that are able to more efficiently relay the magnetic information along the resulting chain.

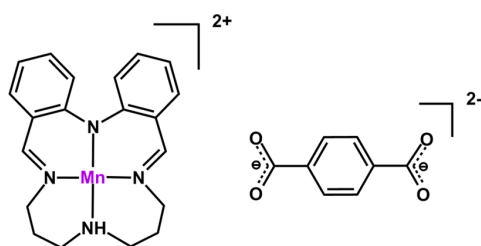
The field of molecular magnetism has been a rapidly expanding research area since the discovery in 1993 of the first single-molecule magnet (SMM),^{1,2} and in 2001 of the first one-dimensional (1D) analogue,³ subsequently named a single-chain magnet (SCM).⁴ Several SCMs have shown promising results, and multifunctional SCMs have also been reported.^{5–21} SMM and SCM compounds are therefore attractive objects for fundamental studies, for example, to explore quantum effects, and for potential applications, such as data storage.^{22,23}

Our approach to SMMs has been to use macrocyclic ligands to provide control and fine-tuning of the metal ion environments,^{24–29} as well as to confer stability and processability on our systems.^{30–35} Following from this, our strategy for accessing SCMs³³ has been to link these macrocyclic SMMs into chains, as a similar approach has been proven to generate SCMs.³⁶ Of course, the formation of a chain does not

guarantee SCM behavior, and unfortunately this was the problem in the case of the systems prepared from our *tetrametallic* 3d-4f macrocyclic [Cu^{II}₃Tb^{III}] SMM building blocks.^{30,35,37} Nevertheless, the macrocyclic approach provides both enhanced stability and more control over the resulting molecular architectures than noncyclic analogues can, so herein a *monometallic* Mn(III) macrocyclic complex, [Mn^{III}(L^{Pr})(NCS)₂] (1), reported earlier,³⁴ has been reinvestigated and found to exhibit slow relaxation of the magnetization. Manganese(III) is usually Jahn–Teller distorted so it provides the required uniaxial anisotropy for

creating a thermal energy barrier that is essential to observe SMM and SCM properties. The organization of these Mn(III) building blocks into 1D coordination polymers often helps to align all the distortion axes, that correspond to local easy axes of anisotropy, along a unique direction, and thus may induce SCM properties when the intrachain magnetic interactions are significant.³⁸ Hence, **1** was chosen for use as a new anisotropic building block, and a terephthalate dianion, [tpa]²⁻, was chosen as a potentially linear linker (Scheme 1). Although no

Scheme 1. Schematic View of the Building Block Moieties: the Dication [Mn^{III}(L^{Pr})²⁺ Building Block of **1 (Left) and the Dianion Linker [tpa]²⁻ (Right)**



SCMs have been reported using [tpa]²⁻ as a linker, a related dianion, pyridine-2,5-dicarboxylate, 2,5-pydc²⁻, has been used, by Gao and co-workers, in the synthesis of 1D coordination polymers [Ln₂Co₂(2,5-pydc)₆(H₂O)₄]_n·2nH₂O (Ln = Dy or Tb) claimed to behave like SCMs.³⁹

The 1D-coordination polymer [Mn^{III}(L^{Pr})(tpa)₂]_n (**2**) was obtained by slow liquid–liquid diffusion together of the two reagent solutions (in 1:1 H₂O/DMF), [Mn^{III}(L^{Pr})(NCS)₂] (**1**)³⁴ and Na₂[tpa]. Dark red crystals of [Mn^{III}(L^{Pr})(tpa)₂]_n·nH₂O·0.5nDMF (**2**) were obtained over a few days, and more formed over the next few weeks (yield 31%).

A single crystal X-ray structure determination on **2** (Figures 1 and S1 and S2; Tables 1 and S1) confirms the 1:1 assembly

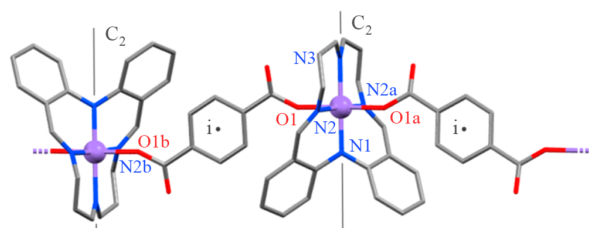


Figure 1. Perspective view of the 1D coordination polymer (chain) [Mn^{III}(L^{Pr})(tpa)₂]_n·nH₂O·0.5nDMF (**2**). All hydrogen atoms and noncoordinating solvent molecules are omitted for clarity. Color code: Mn (violet), O (red), N (blue), and C (gray). Symmetry operations: a = 2-fold axis (C₂) running through N1–Mn1–N3, and b = center of inversion (i) located in the middle of the terephthalate ring.

of a 1D polymer of alternating dicationic macrocycles [Mn^{III}(L^{Pr})²⁺ (from **1**) with dianionic linkers [tpa]²⁻. The chain crystallizes in the monoclinic space group P2₁/n with half a Mn(III) macrocycle and half a [tpa]²⁻ in the asymmetric unit, as well as a disordered water molecule (0.75:0.25) and a half occupancy DMF molecule. The other half of the

Table 1. Comparison of Range and Average Lengths (Å) of Mn–X Bonds (X_{axial} is N for **1 and O for **2**), Selected Angles (deg) and Shortest M···M Separations (Å), and Octahedral Axial Elongation Parameters^a for Both the Building Block (**1**) and the Resulting 1D Polymer (**2**)**

parameters	macrocycle (1)	1D polymer (2)
Mn–N _{amino}	1.922(7), 1.913(7)	1.958(6)
Mn–N _{imine}	2.00(8)–2.031(7)	2.041(4)
Mn–N _{amine}	2.087(7), 2.101(8)	2.075(7)
Mn–N _{eq}	1.913–2.101 (av. 2.012)	1.958–2.075 (av. 2.029)
Mn–X _{axial}	2.203–2.230 (av. 2.218)	2.151
T ⁴⁰	0.91	0.94
X _{axial} –Mn–X _{axial}	176.0(3)–178.8(3)	177.8(2)
Mn···Mn (intrachain)		11.418
Mn···Mn (interchain)	7.976	7.854

^aT = average in plane Cu–N divided by average axial Cu–X; T < 1 for axial elongation vs T > 1 for axial compression.⁴⁰

macrocyclic unit is generated by a 2-fold axis that runs through N1–Mn1–N3, and the other half of the [tpa]²⁻ is generated by an inversion center located in the middle of the terephthalate ring.

The monoanionic tetradentate macrocyclic ligand provides an equatorial plane to the Mn(III) center, comprising one amino, one amine, and two Schiff base nitrogen donors (Table 1). The shortest Mn–N bond involves the deprotonated amino nitrogen atom (Mn–N1 1.958 Å), while the longest is to the neutral amine nitrogen atom (Mn–N3 2.075 Å). The N₄O₂ coordination of the Mn(III) centers is completed by two *trans* coordinated monodentate [tpa]²⁻ anions, which link the complexes in the chain together. As expected for a Mn(III) metal ion, Jahn–Teller elongation is observed, and it occurs along the Mn–O bonds of these terephthalate linkers (Mn–O1 2.151 Å), resulting in a tetragonal elongation (T = 0.94).⁴⁰

Herein the magnetic properties of the 1D compound **2** are investigated, and those of the Mn(III) building block, [Mn^{III}(L^{Pr})(NCS)₂], **1** have been reinvestigated to check for slow relaxation of the magnetization. The χT product is 3.1 cm³ K mol⁻¹ for both **1** and **2** at room temperature (Figure 2), which is in excellent agreement with the expected value for one manganese(III) ion (S = 2; g = 2; C = 3.0 cm³ K mol⁻¹).

Along the chain, each [Mn^{III}(L^{Pr})²⁺ macrocyclic unit is linked to the next by a bis-monodentate bridging terephthalate linker, forming the 1D coordination polymer. Because of the inversion symmetry at the centroid of the linkers, the macrocycles alternate up and down along the chain direction. The 1D polymers pack together efficiently via classical O–H bonds involving the water of crystallization (O30–O2 = 2.952 Å and O30–O50 = 2.732 Å) and nonclassical C–H-bond interactions, some of which involve the DMF of crystallization, O50 (C5′–O2 = 3.422 Å and C9′–O50 = 3.096 Å), resulting in a 3D supramolecular network (Figures S1 and S2, Supporting Information). Unsurprisingly, the Mn···Mn separation is significantly shorter between chains (7.854 Å) than within a chain (11.418 Å).

Upon lowering the temperature, the χT product is roughly constant until around 50 K (**1**) and 40 K (**2**), respectively, when it starts to decrease, reaching minimum values of 1.6 (**1**) and 2.1 (**2**) cm³ K mol⁻¹ at 1.85 K, consistent with the possible combined effects of the magnetic anisotropy intrinsic to Mn(III) metal ions and antiferromagnetic interactions between the macrocyclic units. Using an anisotropic spin Heisenberg

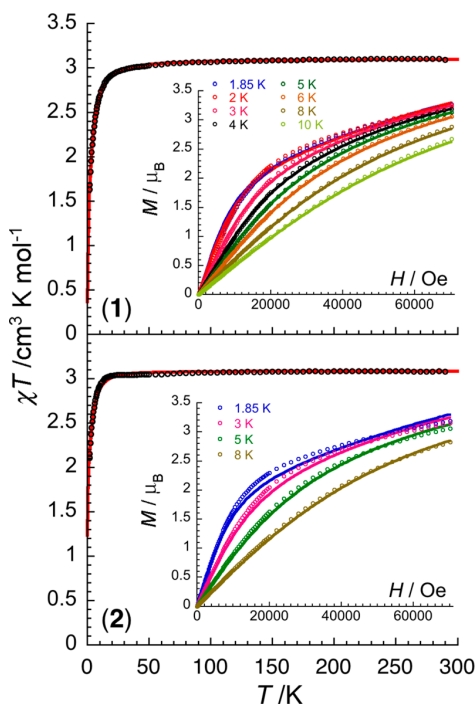


Figure 2. Temperature dependence of the χT product (where χ is the molar magnetic susceptibility that equals M/H per complex) collected in an applied dc magnetic field of 0.1 T for **1** (top) and **2** (bottom). Inset: Field dependence of the magnetization for **1** (top) and **2** (bottom) below 10 and 8 K ($8\text{--}200 \text{ mT min}^{-1}$), respectively. The solid lines are the best fits to the model described in the text.

Hamiltonian ($H = DS_{\text{Mn},z}^2$) and the analytical expression of the magnetization estimated by applying the van Vleck equation^{41,42} in the weak field approximation,^{43,44} the susceptibility and magnetization data could be fitted with $S = 2$, $g = 2.03(2)$, $D/k_B = -5.0(1) \text{ K}$ and, for **1** $zJ/k_B = -0.25(2) \text{ K}$, whereas for **2** $zJ/k_B = -0.04(1) \text{ K}$. Interestingly, the antiferromagnetic coupling (J) is weaker for the 1D compound **2** than for the isolated macrocycle **1**, indicating that, unfortunately, the $[\text{tpa}]^{2-}$ linker separates the $[\text{Mn}^{\text{III}}(\text{L}^{\text{Pr}})]^{2+}$ complexes more efficiently. Both of these fits indicate the presence of the expected magnetic anisotropy of the Mn(III) ion, which is confirmed by the field dependence of the magnetization as the M versus H/T curves do not superimpose at high fields (Figure 2 insets, and Figures S3 and S6, Supporting Information).

The ac susceptibility of macrocyclic Mn(III) building block **1** was measured to check for possible slow relaxation of the magnetization. At 1.85 K, there was no out-of-phase component (χ'') without an external field applied (Figure S4, Supporting Information). However, when an external dc field is applied, an out-of-phase component is observed (Figure S5, Supporting Information), indicating the presence of slow relaxation of the magnetization in the **1** unit. Unfortunately, the relaxation modes are not visible in the temperature/ac frequency window of measurement, so the slow relaxation time could not be quantified. However, it is promising to see that this new building block is an SMM.

The ac susceptibility of the chain **2** was also measured to check for possible slow relaxation of the magnetization. At 1.85 K, there was no χ'' component without an external field applied (Figures S7 and S8, Supporting Information).

However, when an external dc field is applied, an out-of-phase component (χ'') is observed (Figure 3), indicating the

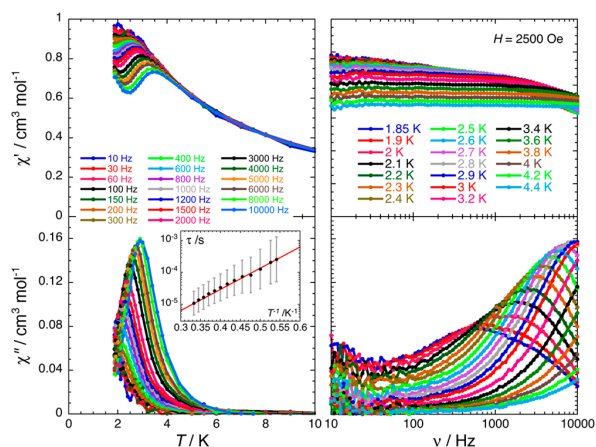


Figure 3. Frequency (left) and temperature (right) dependences of the real (χ' , top) and imaginary (χ'' , bottom) parts of the ac susceptibility, between 1.85 and 10 K and between 10 and 10000 Hz, for **2** in a 2500-Oe dc field. Solid lines are visual guides. Inset (bottom left): τ vs T^{-1} plot at a 2500-Oe dc field from the generalized Debye fit of the frequency dependence of the imaginary part of the ac susceptibility (χ'' ; error bars on the relaxation time have been calculated from the α parameters of the generalized Debye fit and the log-normal distribution; see ref 45). The solid red line is the best fit to the Arrhenius law.

presence of slow relaxation of the magnetization, due to the presence of $[\text{Mn}^{\text{III}}(\text{L}^{\text{Pr}})]^{2+}$ unit (analogous to **1**) in the chain. This time, the relaxation modes are clearly visible in the window of measurement, so the slow relaxation of the magnetization can be quantified, fitting the ac susceptibility data by a generalized Debye model. The temperature dependence of the relaxation time can be fitted to an Arrhenius law with $\Delta_{\text{eff}}/k_B = 15(2) \text{ K}$ and $\tau_0 = 7(2) \times 10^{-8} \text{ s}$ (Figure 3, bottom left, Inset). While this compound is a chain from a structural point of view, the observed slow dynamics of the magnetization cannot be attributed to an SCM behavior as the magnetic interactions between the Mn(III) centers through end-to-end terephthalate bridges along the chain are unfortunately negligible, as shown by the analysis of the dc susceptibility (vide supra) and previously reported systems.⁴⁶ This compound is thus an SMM and not an SCM. Interestingly **2** is a “better” SMM than **1**, as for **1** the relaxation modes were not visible in the experimental window of measurement.

In conclusion, the ac susceptibility of the Mn(III) macrocycle **1** was measured and revealed that it has potential for use as an SMM building block in the synthesis of SCMs. As a first step to test its coordination ability, it has been combined with a terephthalate linker, giving single crystals of the desired 1D coordination polymer **2**. The structure determination showed that the dianionic linker has efficiently aligned the SMM building blocks along the chain, but the magnetic characterization shows that it has not effectively relayed the magnetic information along the 1D chain, leading to magnetically isolated Mn(III) centers. The SMM properties of the macrocyclic Mn(III) unit in this 1D compound have been fully characterized leading to the conclusion that the relaxation time follows a thermally activated process with $\Delta_{\text{eff}}/$

$k_B = 15(2)$ K and $\tau_0 = 7(2) \times 10^{-8}$ s. While compound **2** is not an SCM, it is an SMM, and more importantly the potential of the $[\text{Mn}^{\text{III}}(\text{L}^{\text{Pr}})]^{2+}$ SMM building block (**1**) for SCM synthesis is clear and should be pursued further in the future, but utilizing linkers that can more efficiently relay the magnetic information along the resulting 1D coordination polymer.

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