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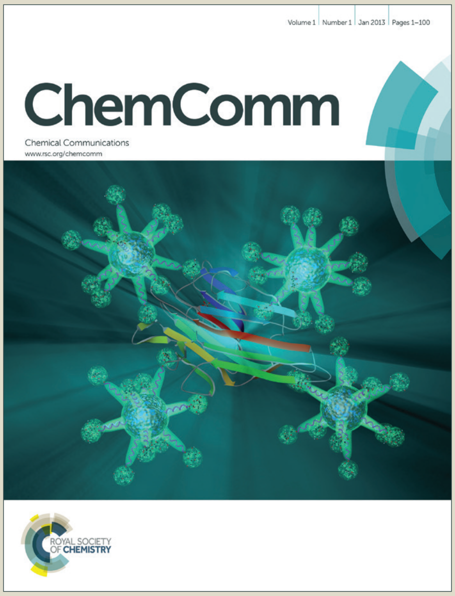

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ARTICLE TYPE

# A Single-Chain Magnet Based on Linear [$Mn^{III}_2Mn^{II}$] units

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**The synthesis, structural characterization and magnetic properties of an 1-D coordination polymer based on a linear mixed valent [$Mn^{III}_2Mn^{II}$] repeating unit is described. It displays Single-Chain Magnet (SCM) behaviour with an energy barrier of ~ 38 K and represents the first example of a mixed valent Mn/carboxylate SCM with a linear architecture.**

Polynuclear Mn/carboxylate complexes and coordination polymers have attracted intense interest for a number of reasons including their novel crystal structures and interesting magnetic properties.[1] Such compounds often behave as Single-Molecule Magnets (SMMs) or Single-Chain Magnets (SCMs) displaying novel magnetic phenomena such as slow relaxation and large hysteresis of magnetisation and quantum tunneling of the magnetisation (QTM).[1-4] SMMs derive their properties from the combination of a large spin ground-state and Ising-type (easy-axis) magnetoanisotropy whereas SCMs possess strong intrachain exchange interactions without spin compensation between high spin anisotropic (Ising-type) units along the chain.[1-3] Such magnetic species are remarkable results of the molecular approach to nanoscale magnetic materials and have been proposed as candidates for applications in high-density information storage, molecular spintronics and quantum computation.[5]

As a result, numerous Mn/carboxylate complexes and SMMs have been reported with a variety of topologies and nuclearities ranging from 2 to 84,[1,6] but in contrast, only a small number of homospin manganese SCMs have been described.[2] The largest category of Mn complexes in the field of molecular magnetism is possibly the trinuclear species since they often display ferromagnetic exchange interactions and SMM behaviour.[1d,7] Such [$Mn_3$] units have also been used as building–blocks or modules for the construction of larger aggregates[1d,8] and multidimensional coordination polymers, which display interesting magnetic properties.[1d,9] Thus, several [$Mn_3$] SMMs and a few [$Mn_3$]$_\infty$ SCMs have been reported with the vast majority of these materials being based on oxido-centered triangular topology.[1d,7-9]

To the best of our knowledge, there are only four linear [$Mn_3$] complexes that have been reported to display SMM behaviour,[10] whereas such moieties have never been observed to form SCM systems. In fact, SCMs consisting of polynuclear Mn/carboxylate linear repeating units are completely unknown. These simple 1-D architectures built from linear modules are particularly interesting since they provide ideal model systems,[2a,b] which could become textbook examples for magnetochemists and physicists, allowing them to go further in the understanding of the SCM theory. Although SCMs with linear architectures are well-known when rigid ligands that impose the geometry of the resultant compound, such as cyanides,[11] are employed, they are very rare in 3d metal carboxylate chemistry.[12, 13]

We herein report the synthesis, crystal structure and magnetic properties of an 1-D coordination polymer [$Mn_3(mpt)_2(EtCO_2)_2(MeOH)_2]_\infty$ (**1**)$_\infty$ ($H_3mpt$: 3-methylpentane-1,3,5-triol), based on a novel linear mixed valent trinuclear [$Mn^{III}_2Mn^{II}$] repeating unit. It displays SCM properties with a thermally activated relaxation time and an energy barrier of about 38 K. This compound represents the first example of (i) a SCM based on a linear $Mn_x$ carboxylate repeating unit and (ii) a mixed valent Mn/carboxylate SCM with a linear architecture.

The solvothermal reaction of $Mn(O_2CEt)_2 \cdot 2H_2O$ and $H_3mpt$ in a ~ 1:2 molar ratio in MeOH at 100°C for 24 h followed by slow cooling to room temperature gave brown rod-shaped crystals of (**1**)$_\infty$ in 35 % yield; dried solid was analysed satisfactorily as (**1**)$_\infty$‡ (for synthetic details see ESI†). The crystal structure‡ of (**1**)$_\infty$ contains an 1-D coordination polymer consisting of a linear trinuclear [$Mn_3(mpt)_2(EtCO_2)_2(MeOH)_2$] (Fig. 1, top) repeating unit. Charge considerations, bond valence sum calculations[14] and inspection of metric parameters indicate that the [$Mn_3$] moiety is mixed-valent containing two $Mn^{III}$ (Mn2 and Mn3) and one $Mn^{II}$ (Mn1) ions with the latter located in the one outer part of the linear [$Mn_3$] unit.

The three Mn ions are held together through one $EtCO_2^-$ group bridging in the usual *syn*, *syn* - η: η: μ fashion the two $Mn^{III}$ ions, and two $\eta^2$: $\eta^2$: $\eta^2$: $\mu_4$ $mpt^{3-}$ ligands. Two μ-OR arms of the latter together with an additional *syn*, *syn* - η: η: μ $EtCO_2^-$ group link the neighbouring [$Mn_3$] units resulting in the formation of the 1-D coordination polymer of (**1**)$_\infty$ (Fig. 1, bottom). The $Mn^{III}$-O-$Mn^{III}$ and Mn2$^{III}$-O-Mn1$^{II}$ angles are ~ 98.4(2)° and ~ 100.5(2)° respectively whereas the Mn3$^{III}$-O-Mn1$^{II}$ one between the neighbouring units of (**1**)$_\infty$ is ~ 97.1(2)°. The peripheral ligation is completed by two terminal methanol molecules connected to the central $Mn^{III}$ (Mn2) and $Mn^{II}$ ions. The Mn ions are in very close proximity along the chain, with Mn···Mn separations of 3.120, 2.904 and 3.038 Å for Mn1···Mn2, Mn2···Mn3 and Mn3···Mn1, respectively. All Mn ions are six- coordinated adopting a distorted octahedral geometry with the two $Mn^{III}$ ions displaying the expected Jahn- Teller elongation axes (O7-Mn2-O10 and O8-

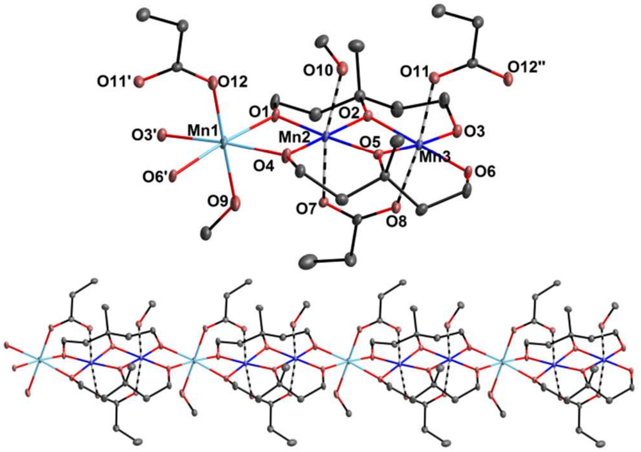

**Fig. 1** ORTEP-like view of the repeating unit (top) and a part of the one-dimensional structure in $(\mathbf{1})_\infty$ (bottom) with thermal ellipsoids fixed at 50 %. Colour code: $Mn^{II}$, cyan; $Mn^{III}$, blue; O, red; C, grey. The H atoms are omitted for clarity. The $Mn^{III}$ Jahn-Teller axes are in dashed bonds.

Mn3-O11) which are nearly co-parallel (the angle between the JT axes is ~7.6(1)°). These JT axes involve donor atoms either from methanol or propionate ligands and thus all equatorial coordinating positions of the $Mn^{III}$ ions are occupied by the alkoxido O atoms of the two $mpt^{3-}$ ligands. It is also noticeable that the Mn ions within the chain are nearly co-linear with intrachain Mn-Mn-Mn angles being in the 170 - 180° range. Examination of the crystal packing reveals that the chains run parallel to the *a* axis and there is no significant inter-chain hydrogen bonding interactions (Fig. S1, ESI†). Thus, the neighbouring chains are well separated, with the interchain Mn···Mn separations being all superior to 8.27 Å.

The 1-D coordination polymer found in $(\mathbf{1})_\infty$ displays several attractive and unique structural features. In particular, $(\mathbf{1})_\infty$ is the first example of a coordination polymer, and rare example of metal complex in general, containing the $H_3mpt$ ligand in its neutral or anionic form.[15] In addition, its structural architecture that can be described as a linear array of $Mn^{2+}$ and $Mn^{3+}$ ions tightly connected through both mono- and poly-atomic bridges ($RO^-$ and $EtCO_2^-$ respectively), is unprecedented in Mn/carboxylate chemistry, although some chains consisting of mononuclear repeating units have been reported.[12,16] Such compounds, especially those containing one or more trivalent Mn ions like in $(\mathbf{1})_\infty$, are particularly attractive for the area of molecular magnetism since they could display SCM properties induced by the intrisic magnetic anisotropy of their $Mn^{III}$ centers.

The magnetic properties of $(\mathbf{1})_\infty$ were investigated as a function of temperature (1.8-270 K) using *dc* magnetic field up to 7 T. A plot of $\chi T$ versus $T$ for $(\mathbf{1})_\infty$, collected at 1000 Oe, is shown in Fig. 2. The $\chi T$ value steadily decreases from 7.9 $cm^3\ mol^{-1}$ K at 270 K to 4.7 $cm^3\ mol^{-1}$ K at 34 K and then rapidly increases to 6.8 $cm^3\ mol^{-1}$ K at 4 K before it drops down to 5.5 $cm^3\ mol^{-1}$ K at 1.85 K. The room temperature $\chi T$ product is significantly smaller than the spin-only ($g = 2$) value of 10.375 $cm^3\ mol^{-1}$ K expected for one $Mn^{II}$ and two $Mn^{III}$ non-interacting centers. The overall profile of the $\chi T$ versus $T$ plot for $(\mathbf{1})_\infty$ reveals the existence of competing ferromagnetic and antiferromagnetic exchange interactions within the chain, the latter being responsible for the low $\chi T$ product at 270 K. The $\chi T$ value around 40 K suggests a virtual spin ground state of $S_T = {}^5/_2$ for the $[Mn^{III}_2Mn^{II}]$ repeating unit induced by significant antiferromagnetic interactions while the increase below 40 K reveals probably ferromagnetic interactions between these trinuclear magnetic moieties. The decrease of the $\chi T$ value below 4 K is likely due to the existence of weak antiferromagnetic interchain interactions, magnetic anisotropy and Zeeman effects from the applied field.

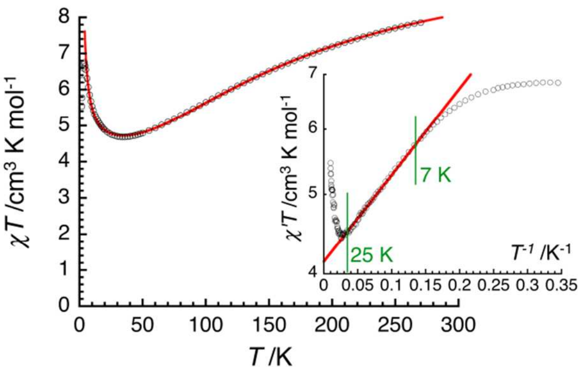

**Fig. 2** Temperature dependence of $\chi T$ product ($\chi$ is the magnetic susceptibility per $[Mn_3]$ unit at 1000 Oe) between 1.8 and 270 K for a polycrystalline sample of $(\mathbf{1})_\infty$ (Fig. S2, ESI†). The solid red line is the best fit of the experimental data to the chain model (see text). Inset: semi-logarithmic $\chi' T$ versus $T^{-1}$ plot ($\chi'$ being the in-phase ac susceptibility in zero *dc* field at 100 Hz and $H_{ac}$ = 3 Oe) with the best fit (red solid line) using the 1-D Ising model between 7 and 25 K.

In order to quantify the strength of the intrachain interactions in $(\mathbf{1})_\infty$, the magnetic susceptibility has been modeled using the following classical spin chain Hamiltonian:

$$\mathbf{H} = -2\sum_{i=1}^{N} J_1\left(\vec{S}_{1,i}\cdot\vec{S}_{A,i}\right) + J_2\left(\vec{S}_{A,i}\cdot\vec{S}_{B,i}\right) + J_1'\left(\vec{S}_{B,i}\cdot\vec{S}_{1,i+1}\right)$$

with $J_1$ and $J_1'$ being the two different $Mn^{II}$-$Mn^{III}$ magnetic interactions, $J_2$ being the $Mn^{III}$-$Mn^{III}$ coupling, $S_{1,i} = {}^5/_2$ and $S_{A,i} = S_{B,i} = 2$. Fisher's approach[17] was extended to establish an analytical expression of the low field susceptibility of this 1-D system (see supporting information). Between 5 and 270 K, an excellent fit of the experimental data was obtained with $J_1/k_B$ = -11(1) K, $J_2/k_B$ = -20(1) K, $J_1'/k_B$ = +0.23(5) K and $g$ = 2.00(5) (Fig. 2).[18] The existence of moderate antiferromagnetic exchange for the $[Mn^{III}(\mu\text{-}OR)_2(O_2CEt)Mn^{III}]$ unit with the two ($\mu$-OR) in equatorial position is in perfect accordance with results reported for analogous systems.[19] On the other hand, it is very difficult to assign the $J_1$ and $J_1'$ interactions to the $[Mn^{III}(\mu\text{-}OR)_2(O_2CEt)\text{-}Mn^{II}]$ or $[Mn^{II}(\mu\text{-}OR)_2Mn^{III}]$ pathways. Although, it is tempting to assume that the former one is ferromagnetic due to more acute $Mn^{III}$-O-$Mn^{II}$ angles (97.1° versus 100.5°), the facts that the two units are different and also that there is no magnetostructural study for such linkages with similar metric parameters, do not allow us to confidently conclude on the assignment.[10a,20] But in both cases, this magnetic system can be viewed at low temperatures as a chain of $S_T = {}^5/_2$ $[Mn^{III}_2Mn^{II}]$ units in weak ferromagnetic interactions. In order to test further the 1-D nature of the magnetic properties in $(\mathbf{1})_\infty$, the temperature dependence of the correlation length, $\xi$, was estimated from the magnetic susceptibility. In any 1-D classical systems, $\xi$ is directly proportional to $\chi' T$ ($\chi'$ being the zero field susceptibility).[2a,17,21] For an Ising-like or anisotropic Heisenberg spin chain, the $\chi' T$ product follows a thermally activated behaviour: $\chi' T \approx$

$C_{\mathrm{eff}}\times\exp(\Delta\xi\ /k_{\mathrm{B}}T)$ ($C_{\mathrm{eff}}$: the effective Curie constant; $\Delta\xi$: the energy to create a domain wall along the chain).[2a] Confirming the 1-D Ising-like character of the magnetic properties, the $\ln(\chi'T)$ versus $1/T$ (inset Fig. 2) features a linear region between 7 and 25 K with $\Delta\xi$ equal to 2.5 K. Notably, $\Delta\xi$ is smaller (but still of the same order of magnitude) than the theoretical value in the Ising limit:[2a] $\Delta\xi\ /k_{\mathrm{B}} = 4J_{\mathrm{eff}}S_{\mathrm{T}}^2/k_{\mathrm{B}} = 4.6 \pm 1$ K (with $J_{\mathrm{eff}}S_{\mathrm{T}}^2 = J_1'S_1S_{\mathrm{A}}$). The reduction of $\Delta\xi$ is likely induced by low lying excited states above the $S_{\mathrm{T}} = {}^5/_2$ ground state and also by a possible departure from the Ising limit. Nevertheless, the 1-D magnetic properties of $(\mathbf{1})_\infty$ are clearly established. In addition, with the presence of non-compensated spins along the chain, which is also composed of anisotropic repeating units, all the ingredients seem to be present in $(\mathbf{1})_\infty$ to observe a SCM behaviour.[2a,2c] Therefore, even if the *M* versus *H* data (Fig. S3, ESI†) did not show any sign of hysteresis effect (at 100-400 Oe/min), *ac* susceptibility measurements were performed to probe the magnetisation dynamics. The *ac* data, shown in Fig. 3, reveal a strong frequency dependence of both in-phase ($\chi'$) and out-of-phase ($\chi''$) signals below 4 K indicating the existence of slow relaxation of the magnetisation in $(\mathbf{1})_\infty$. The temperature dependence of the magnetisation relaxation time, $\tau$ was deduced from the out-of-phase data (versus $T$ and $\nu$) as shown in Fig. 3 inset.

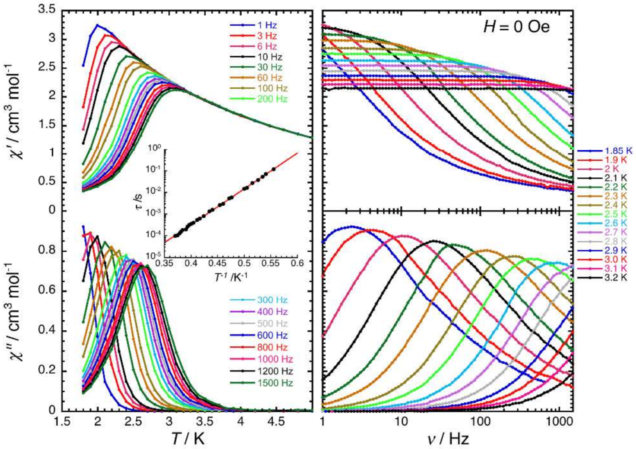

**Fig. 3** Temperature (1.86-5 K; left) and frequency (1-1500 Hz; right) dependence of the real ($\chi'$, top) and imaginary ($\chi''$, bottom) parts of the ac susceptibility for $(\mathbf{1})_\infty$ in zero *dc*-field (with $H_{\mathrm{ac}} = 3$ Oe). Solid lines are visual guides. Inset: Relaxation time ($\tau$) versus $T^{-1}$ plot in zero *dc*-field for $(\mathbf{1})_\infty$. The red solid line is the fit to the Arrhenius Law.

The $\tau$ versus $1/T$ data were fitted to the Arrhenius equation $\tau = \tau_0\ \exp(\Delta\tau/k_{\mathrm{B}}T)$ (where $\Delta\tau$ is the energy barrier to reverse the magnetisation of a chain and $\tau_0$ is the intrinsic reversal time of the magnetically isolated spin unit of the chain in contact with the thermal bath) with $\Delta\tau/k_{\mathrm{B}} = 38$ K and $\tau_0 = 8.0 \times 10^{-11}$s, the latter value being in good agreement with those encountered for reported SCMs.[2,11,12] Considering that the correlation length, $\xi$, ($\propto\chi'T$) is saturating around 3 K (Fig. 2), the observed dynamics of the magnetisation (below 3 K; Fig. 3) have been measured in the finite-size regime of SCM relaxation.[2a,2c] Therefore the anisotropy barrier ($\Delta_{\mathrm{A}}$) can be estimated at 35.5 K from $\Delta\xi$ and $\Delta\tau$, as in this regime $\Delta\tau = \Delta\xi + \Delta_{\mathrm{A}}$. This significant value of the magnetic anisotropy energy is in good agreement with the lack of saturation of magnetisation at fields up to 7 T (Fig. S3, ESI†).

In conclusion, the use of the triol $H_3$mpt in Mn/carboxylate chemistry afforded a 1-D coordination polymer, $(\mathbf{1})_\infty$, consisting of tightly connected $[\mathrm{Mn^{III}}_2\mathrm{Mn^{II}}]$ linear repeating units. For only second time in the family of Mn/carboxylate chains with linear structural architecture and the first time for mixed valent ones, this system exhibits SCM properties with an appreciable relaxation energy barrier of 38 K. It should also be pointed out that the mpt$^{3-}$ ligand plays a crucial role not only in the formation but also in the appearance of SCM behaviour in $(\mathbf{1})_\infty$. In particular, its alkoxido bridging arms occupied all equatorial positions of the Mn ions directing the terminal solvent and carboxylate ligands to the axial ones thus contributing in the alignment of the local easy magnetic axes of the Mn$^{\mathrm{III}}$ ions along the chain direction. Thus, this work reveals that $H_3$mpt could be proven invaluable for the isolation of novel carboxylate-based SCMs with simple spin and interaction topologies.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: Crystallographic data (CIF format) for $(\mathbf{1})_\infty$ and various structural and magnetism figures. CCDC reference number 1015476. See DOI: 10.1039/b000000x/

‡ Vacuum-dried solid analysed (C, H, N) as $(\mathbf{1})_\infty$. Calcd. (Found): C, 37.69 (37.82); H, 6.33 (6.01) %. Crystal data for $(\mathbf{1})_\infty$: $C_{20}H_{40}Mn_3O_{12}$, *M*w = 637.34 g mol$^{-1}$, triclinic space group $P\bar{1}$, $a = 9.0326(8)$ Å , $b = 9.208(2)$ Å , $c = 17.277(2)$ Å, $\alpha = 102.92(2)^{\circ}$, $\beta = 91.393(9)^{\circ}$, $\gamma = 111.20(1)^{\circ}$, $Z = 2$, $V = 1297.0(3)$ Å$^3$, $T = 100(2)$ K, $\rho_{\mathrm{calcd}} = 1.632$ g cm$^{-3}$, 7567 reflections collected, 3361 reflections used, $R_1\ [I > 2\sigma(I)] = 0.0476$, w$R_2 = 0.1410$.
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