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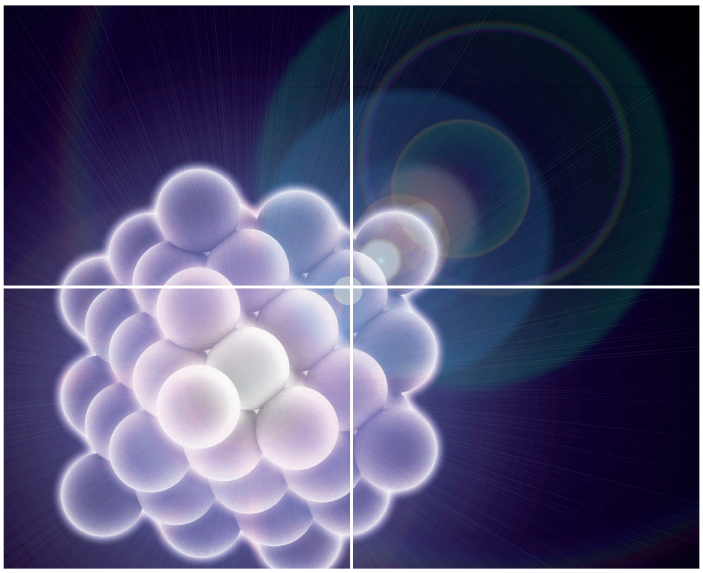

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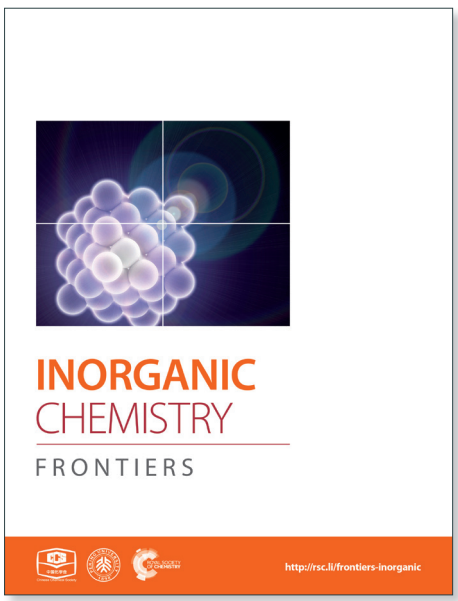


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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE

# Field-Induced Dynamic Magnetic Behaviour of a Canted Weak Ferromagnetic Chain Material

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***Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X***
**DOI: 10.1039/b000000x**

An interesting 1-D magnetic chain material was facilely synthesized with one-pot route. The $[Mn^{III}_3O]$ based chain shows slow relaxation of magnetization in different applied fields, even in the antiferromagnetic ordered phase. Furthermore, the material amazingly exhibits the coexistence of spin glass, spin canting, and metamagnetic behaviours.

## Introduction

Low-dimensional materials with slow relaxation of magnetization, such as 0-D single-molecule magnets (SMMs)[1] and single-ion magnets (SIMs),[2] as well as 1-D single-chain magnets (SCMs),[3,4] have attained ongoing and great interests for their potential applications in information storage and academic research on molecular magnetism. Furthermore, 1-D magnets can also provide appropriate examples to investigate a few fundamental phenomena in magnetism, such as spin canting,[5-10] metamagnetic transition,[6,7,10] spin flop (SF) transition,[6,10] and spin glass (SG) behaviour.[8-11]

Noncollinear spin arrangements on two sublattices lead to spin canting, whose spins are canted by a small angle due to the asymmetric exchange. As for spin glass, the spins are random distribution originating from the competing interactions, and the metastable frozen state appears at a particular temperature without conventional magnetic long-range ordering.[5,10,11] Apart from the superparamagnets, spin glass also exhibits the slow relaxation behavior, which may have potential applications in information theory, associative memories, and combinatorial optimization.[9] If the interactions are antiferromagnetic (AF) with magnetic anisotropy, the spin flop could happen under the applied magnetic field parallel to the easy-axis, giving rise that the spins flop to the direction perpendicular to the field and then point to it more and more until the spins line up with the field.[5,6,10] If the preference of the magnetic moments is strong enough, spin flip should happen instead of spin flop.[5]

Although these phenomena (spin canting, spin glass behaviour, and metamagnetism) are distinguishing in many aspects, they also share some common points in nature, such as the existence of the magnetic anisotropy.[5] The coexistence for two of them are particularly rare,[8a,10] not to mention the simultaneous presence of all of them in one single magnetic system.

Herein, we report an interesting 1D chain material based on $[Mn^{III}_3O]$ units which exhibits different magnetic behaviours (spin canting, spin glass, and metamagnetism) under different magnetic fields and temperatures. At zero field, the coexistence of weak ferromagnetism and slow relaxation behaviour (spin glass behaviour) is dominated. Althought an antiferromagnetic ordering is clearly observed in the spin flop phase, the slow magnetic relaxation doesn't disappear, suggesting a 3-D antiferromagnetic order cannot prevent the slow relaxation of the magnetization.[16] In addition, under a magnetic field strong enough, we can observe the metamagnetic transitions, suggesting a large field can overwhelm the AF interactions and force the spins to align parallel to the field. Consequently, the antiferromagnetic ordering disappears whereas the slow relaxation behaviour still declares its existence.

## Experimental Section

Synthesis of **1**: A mixture of 2-hydroxy-5-methylisophthalaldehyde (33 mg, 0.2 mmol), hydroxylamine hydrochloride (28 mg, 0.4 mmol) and triethylamine (61 mg, 0.6 mmol) in $CH_3OH$ (20 mL) were stirred half an hour. It was then $Mn(OAc)_2 \cdot 4H_2O$ (49 mg, 0.2 mmol) were added. The resulting solution turned greenish black after stirring under ambient conditions for more than 2 hours, and then filtered. Lamellate greenish black crystals of **1** (~33% yield) were obtained until the solution nearly dried. Anal. calcd for $C_{30}H_{38.5}Mn_3N_3O_{18}$ (911.47): C 39.53, H 4.42, N 4.61; found: C 39.18, H 4.61, N 4.97. IR (KBr): ν = 3416 (br), 2922 (m) , 2515 (w) , 2361 (s) , 1663 (s) , 1547 (vs) , 1448 (vs) , 1313 (s) , 1230 (s) ,1049 (s) , 879 (m) , 771 (m) , 667 (s) , 540 (w).

The intensity data of **1** was recorded on a Rigaku R-AXIS SPIDE IP system with Mo$K_\alpha$ radiation ($\lambda$ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares on $F^2$ using SHELXTL.[17a] The disordered water and methanol molecules could not be modelled properly; thus, the program SQUEEZE,[17b] a part of the PLATON package of crystallographic software, was used to calculate the solvent disorder area and remove its contribution to the overall intensity data.

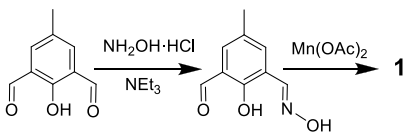
Crystal data of **1**: $C_{30}H_{40}Mn_3N_3O_{19}$, $M$ = 911.47, monoclinic, $a$ = 58.419(6) Å, $b$ = 20.302(2) Å, $c$ = 7.4801(8) Å, $\beta$ = 91.105(3) °, $V$ = 8870.1(17) Å$^3$, $T$ = 100(2) K, space group $C2/c$, $Z$ = 8, $\mu$(Mo$K_\alpha$) = 0.911 mm$^{-1}$, 18929 reflections measured, 8360 independent reflections ($R_{int}$ = 0.0979). The final $R_1$ values were 0.0800 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.2236 (all data). The goodness of fit on $F^2$ was 0.905.

CCDC-832674 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

## Results and discussion

After the oxime was synthesized *in situ*, it was added to $Mn(OAc)_2$ ·$4H_2O$ and triethylamine in methanol (Scheme 1 and Experimental Section). Compound **1** crystallizes in the monoclinic space group, $C2/c$ (see Experimental Section†). All the manganese ions are trivalent, which are confirmed by bond-valence-sum (BVS) calculations (Table S1),[12] charge considerations, and the observation of Jahn-Teller distortion around the Mn$^{III}$ centers.

As can be seen in Fig. 1, compound **1** is composed of *anti-anti* acetate bridged [Mn$^{III}_3$O(mpox)$_3$(H$_2$O)$_3$]$^+$ trigonal units, which are formed by one sharing $\mu_3$-oxo center and three oxime-group (NO) edges. An acetate bridge coordinates two different Mn$^{III}$ ions in the neighbouring [Mn$^{III}_3$O] units. Both of the two Mn$^{III}$ adopt the distorted octahedral geometries, while another one is a distorted square pyramid. No any symmetry elements can be found in the [Mn$^{III}_3$O] unit. Interestingly, the dihedral angle between the adjacent [Mn$^{III}_3$] planes within the chain is 0 °, in other word, they are completely parallel, and the Jahn-Teller axes of Mn$^{III}$ ions are nearly perpendicular to the plane. It is quite different from the previously reported 1-D chains based on [Mn$^{III}_3$O].[13] Supramolecular interactions are also observed - the dimer-like double chain structures are formed in aggregation of neighbouring chains through π-π interactions (3.77 Å, Fig. 1). The shortest interchain distance based on the nearest central oxygen atom of the [Mn$^{III}_3$O] units is 7.373 Å. Moreover, the dihedral angle between each [Mn$^{III}_3$O] plane of the neighbouring chain, namely the dimer-double chain, is 54.8 ° rather than parallel to each other.




**Scheme 1**. Synthetic route of **1**.

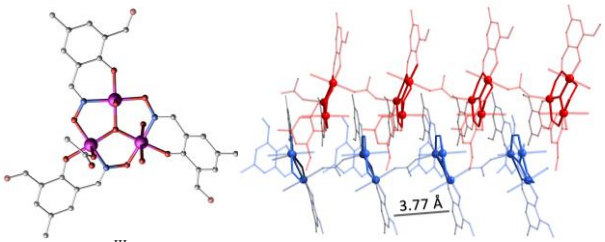



**Figure 1**. [Mn$^{III}_3$O] unit (*left*) and the dimer-like double chain structures (*right*).

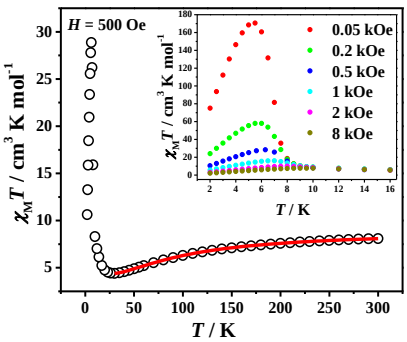



**Figure 2**. The temperature dependence of $\chi_M T$ measured in an applied field of 500 Oe on a powder sample of **1**. The red line is the result of a best fit between 30 and 300 K. Inset: The temperature dependence of the magnetic susceptibility of **1** measured between 2 and 16 K at the indicated applied fields.

The $\chi_M T$ product under a 500 Oe applied dc field in the temperature range of 2-300 K is shown in Fig. 2. The $\chi_M T$ value decreases from 8.09 cm$^3$ K mol$^{-1}$ at 300 K, which is somewhat smaller than the expected value of three spin-only Mn$^{III}$ ions (9.00 cm$^3$ K mol$^{-1}$, taking $g$ = 2.0),[5a,5b,14] to 4.40 cm$^3$ K mol$^{-1}$ at 30 K, suggesting the dominant antiferromagnetic interactions. On further lowering the temperature, the $\chi_M T$ product increases to a maximum of 28.86 cm$^3$ K mol$^{-1}$ at 6.3 K and then drops down to 10.62 cm$^3$ K mol$^{-1}$ at 2 K. The magnetic exchange constants were extracted by the isosceles triangle model[5a,5b,14] in the temperature range of 30-300 K:

$$\hat{\boldsymbol{H}} = -2J_1 (\hat{\boldsymbol{S}}_1 \cdot \hat{\boldsymbol{S}}_2 + \hat{\boldsymbol{S}}_1 \cdot \hat{\boldsymbol{S}}_3) - 2J_2 \hat{\boldsymbol{S}}_2 \cdot \hat{\boldsymbol{S}}_3$$

with the addition of an inter-unit interaction (including intra-chain interaction and inter-chain interaction) by the mean-field approximation ($zJ$), giving $J_1$ = -2.41 cm$^{-1}$, $J_2$ = -9.06 cm$^{-1}$, $zJ$ = 1.39 cm$^{-1}$ and $g$ = 2.01 with $R$ = 2.3 × 10$^{-6}$. The magnetic exchange constants are in the range of the previous [Mn$^{III}_3$O] based analogues ($J_1$: -5.04~-0.38 cm$^{-1}$; $J_2$: -9.51~-1.37 cm$^{-1}$; $zJ$: -0.059~3.94 cm$^{-1}$).[13] The reconstructed zero-field energy levels of the isolated [Mn$^{III}_3$O] unit are shown in Fig. S1, indicating the first excited state of $S$ = 1 is only 3.66 cm$^{-1}$ above the spin ground state of $S$ = 2. The results indicate the presence of competing intra-unit antiferromagnetic interaction and inter-unit ferromagnetic interaction. In addition, the intra-chain interaction among the [Mn$^{III}_3$O] units should be ferromagnetic, because $zJ$ > 0 while the inter-chain interaction is antiferromagnetic (*vide infra*). The phenomenological fitting method may not be very accurate, but still can provide some helpful information for qualitative analysis.

To investigate the phase transition at low temperature, the field-cooled (FC) and zero-field-cooled (ZFC) magnetization measurements were performed at 10 Oe in the 1.8-15 K range (Fig. S2). The FC curve shows an abrupt increase with decreasing temperature below 8 K, reaching saturation at lower temperatures, while the ZFC curve shows a peak. The FC and ZFC data are divergent below the critical temperature $T_C$ = 6.4 K, which indicates the occurrence of irreversibility of magnetization below this temperature. FC magnetizations were measured under different applied fields and obviously field-dependent: the products of susceptibilities increase as the measuring fields decrease. This is an important feature of weak ferromagnetism due to spin-canting, which is attributed to the existence of an antisymmetrical component of the superexchange interaction (Dzyaloshinsky-Moriya interaction) and/or the appropriate magnetic anisotropy, arising from the non-collinear spin arrangements.[5] A remarkable hysteresis loop can be clearly seen at 1.8 K (Fig. 3), confirming the occurrence of spontaneous magnetization, in agreement with the observed spin canting behavior. The coercive field and the remnant magnetization are very large, reaching respectively $H_C$ = 5.4 kOe and $M_R$ = 0.44 $\mu_B$. Thus the canting angle $\alpha$ is estimated to be around 2.1 ° from the equation $\sin(\alpha) = M_R/M_S$ (taking $M_S$ = 12 $\mu_B$).[5]

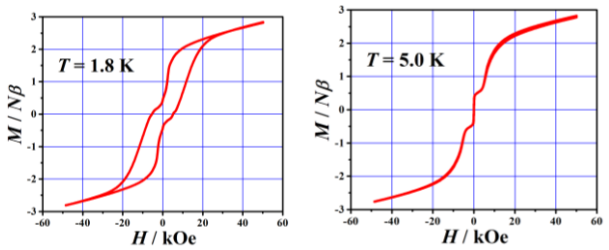



**Figure 3**. The hysteresis loop at 1.8 K (*left*) and 5.0 K (right) on a powder sample of **1**.

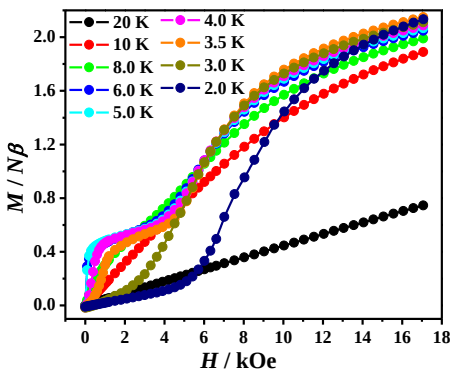



**Figure 4**. The field dependence of the magnetization of a powder sample of **1** obtained at the indicated temperatures. The lines are guided by eyes.

The field-dependence magnetization at different temperatures display pronounced sigmoidal shape (Fig. 4), owing to the field-induced metamagnetic behaviour (spin flop or spin flip). The calculated derivatives of d*M*/d*H* also show field-induced spin-reorientation transition at a critical field (Fig. S3). On closer inspection of the field dependence of the magnetization, something interesting can be found: 1) the magnetization increases nearly linear at high temperature, thus no phase transitions are observed; 2) in the temperature range of 8-5 K, the magnetization increases rapidly at the very beginning, and then increase very slow and remain roughly constant. Under applying a magnetic field larger than $H_C$ obtaining from the maximum (~ 5.5 kOe) of d*M*/d*H*, the magnetization increases again; 3) at low temperature range (4-3 K), the demonstration of the double sigmoidal shape of magnetization and two peaks in d*M*/d*H* suggests two step magnetic phase transitions are occurred, or just corresponding to different field orientations, easy or intermediate axis of magnetization. In order to clarify the present behaviour, a lot of magnetic measurements, like orient a single big crystal in the eigen directions, are necessary in the follow-up work. We infer the presence of metamagnetic transitions accompanied with the increasing magnetic field, and finally the antiferromagnetic interactions among $Mn^{III}$ ions are overwhelmed by the field; 4) a typical sigmoidal shape magnetization is shown at 2 K, also suggesting the presence of metamagnetism.

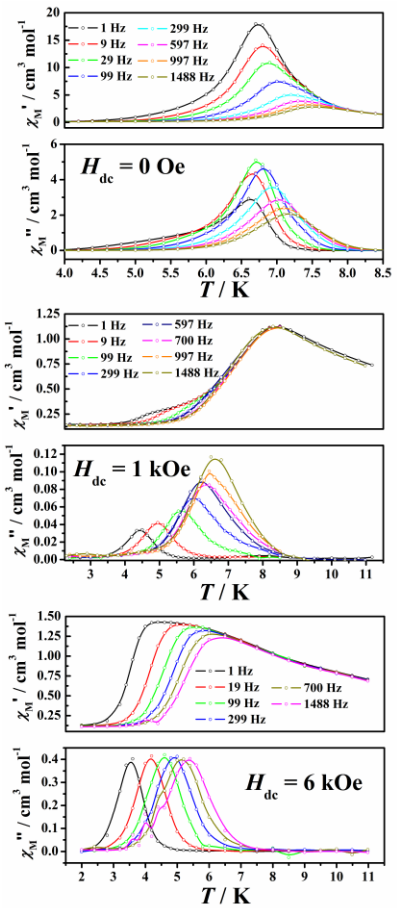



**Figure 5**. Temperature dependence of the ac susceptibilities under 0 Oe (*top*), 1 kOe (*middle*) and 6 kOe (*bottom*) dc fields.

In order to further investigate the phase transitions as well as the slow dynamic behaviours of compound **1**, the ac susceptibilities were measured under different dc fields (Figs. 5, S4, S5). Under zero dc field, both of the in-phase ($\chi_M$') and out-of-phase signals ($\chi_M$'') display a small but significant frequency-dependent behaviour. According to $\varphi = (\Delta T_p/T_p)/\Delta(\log f)$, the

value of $\varphi$ is 0.06 (Fig. S6), suggesting a slow relaxation process of spin-glass-like behaviour.[11] The least-squares fitting of the experimental data to the Arrhenius law typically gives values of $\tau_0 = 2.94 \times 10^{-19}$ s and $\Delta/k_B = 245(5)$ K (Fig. S7). The unusual small pre-exponential factor suggest that the domain walls are difficult to move, and confirm the spin glass behavior.[10,13] The Cole-Cole plots are shown in Fig. S8, yielding the α values in the range of 0.21-0.38 with a generalized Debye model, which corresponds to a moderate distribution of relaxation times.[15] As the existence of simultaneous ferromagnetic and antiferromagnetic exchange couplings, especially the antiferromagnetic exchanges within the $[Mn^{III}_3O]$ asymmetric triangle, it may display some degree of frustration in the magnetic lattice. The randomness in the magnetic lattice is also likely to come from the comparable antiferro/ferro-mangetic interactions, crystal defects and/or the presence of two different coordination environments of the $Mn^{III}$ ions. Thus it makes sense that the material exhibits spin-glass behaviour under zero dc field.

When 1 kOe dc field was applied, a strong frequency-dependent behaviour was observed. Moreover, a non-frequency-dependent cusp appears at 8.35 K in the in-phase susceptibilities, indicating the occurrence of the long-range ordering below the Néel temperature ($T_N$) due to the antiferromagnetic inter-chain interaction and the field-induced spin flop transition. It is reasonable that a small external field can force the magnetization direction tilts slight along with the applied field instead of randomness. After being free from spin glass state, a spin flop happens: an applied magnetic field parallel to the easy axis forces the spins flop to the direction perpendicular to it, and then the magnetic moments get progressively tilted until lining up with the external field. Surprisingly, obvious frequency-dependent out-of-phase signals were still observed. And the calculated $\varphi$ value is 0.11 (Fig. S6), which is close to the superparamagnet-like behaviour. It once again confirms the magnetic field overcomes the randomness of the magnetization. So, it is likely that this compound falls in the category of materials displaying both a magnetic ordered and a magnet-type behaviour. The magnet-type behaviour originates from the chains exhibiting SCM-like behaviour if the chains are isolated, while the antiferromagnetic inter-chain interaction makes the presence of antiferromagnetic ordering.[10b,13b,16] The best-fit parameters of $\tau_0$ and $\Delta/k_B$ of respectively $5.21 \times 10^{-11}$ s and 96.5(2) K (Fig. S7) are acceptable for the SCM-like compounds.[3,10b,13b] The α values extracted by a generalized Debye model are in a moderate distribution of relaxation times in the range of 0.24-0.34 (Fig. S8).

After the magnetic field increases up to 6 kOe, the non-frequency-dependent cusps in the in-phase susceptibilities disappear, instead, the strong frequency-dependent signals in both of in-phase and out-of-phase susceptibilities appear.[10b,13b,16] When a large enough external field (critical field, $H_C$) was employed, the magnetization direction progressively turn parallel to the field, finally resulting the SF-PM transition. In order to check whether the compound behaves like superparamagnet or not at 6 kOe, the $\varphi$ value is calculated, which is as the same as the value at 1 kOe (0.11) (Fig. S6), revealing the superparamagnet-like dynamics behavior. The peak temperatures of $\chi_M$'' can be fitted well to the Arrhenius law, with physically reasonable values of $\tau_0 = 1.13 \times 10^{-10}$ s and $\Delta/k_B = 76(4)$ K (Fig. S7). The α values extracted by a generalized Debye model are also in a moderate distribution of relaxation times in the range of 0.24-0.34 (Fig. S8). In this case, the material also exhibits slow relaxation of magnetization at the magnetic fields larger than $H_C$.

Hence, we can preliminarily conclude as follows: 1) at high temperature or high magnetic field (see Fig. 6, PM phase regime), the thermal perturbation or strong magnetic field provides a large enough energy to overcome the spontaneous alignment of the spins, so the material behaves as paramagnet or superparamagnet; 2) at a medium temperature and a medium field (see Fig. 6, SF phase regime), spin flop transition as well as slow magnetization relaxation clearly occurs in the antiferromagnetic ordered phase; 3) at very low magnetic field (see Fig. 6, SG phase regime), as a result of the possible Dzyaloshinsky-Moriya interaction or the magnetic anisotropy of $Mn^{III}$ ions which lead to spin canting and some degree of frustration due to the completing interactions, both the random alignment of the spins and the creation of the domain walls make the material behaves as spin glass; 4) at a very low temperature (see Fig. 6, PM phase regime), althought the spins are frozen, they can suddenly flip parallel to the magnetic field, triggering the metamagnetic transition in case of increasing the applied field up to large enough.

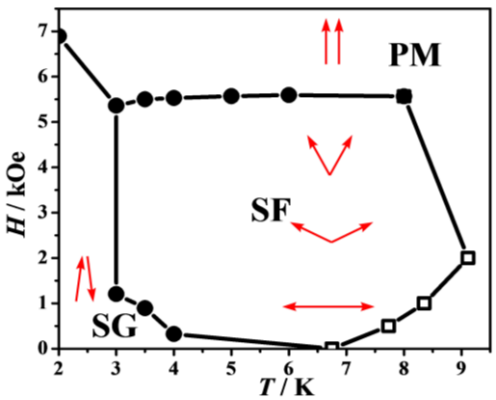



**Figure 6**. *H-T* phase diagram for **1**. ●: Location of the maximum of temperature-dependent differential susceptibility from d*M*/d*H* vs *H* data (Fig. S3); □: Location of the maximum of ac susceptibility from field-dependent $\chi_M$' vs *T* data (Fig. S4).

## Conclusions

In this study, we facilely synthesized a 1-D chain with one-pot route. The $[Mn^{III}_3O]$ based chain shows slow magnetic relaxation with/without different applied fields, even in the antiferromagnetic ordered phase. Furthermore, the material amazingly exhibits the complicated behaviours: the coexistence of spin glass, spin canting, and metamagnetic behaviours. More experiments and further investigations are necessary to deepen our understanding on this interesting material.

## Acknowledgements

This work was supported by the "973 Project" (2014CB845602 and 2012CB821704), the NSFC (Grant nos 91122032, 21371183 and 91422302), the NSF of Guangdong (S2013020013002), Program for Changjiang Scholars and Innovative Research Team in University of China and the Fundamental Research Funds for

the Central Universities. We are grateful to Dr. Rodolphe Clérac for meaningful discussions.

## Notes and references

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‡ Electronic Supplementary Information (ESI) available: The ESI contains additional crystallography tables and figures of magnetic properties. See DOI: 10.1039/b000000x/


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**TOC**

The 1-D $[Mn^{III}_3O]$ based magnetic chain material amazingly exhibits the coexistence of spin-glass, spin-canting, and metamagnetic behaviours as well as slow relaxation of magnetization in different applied fields.