Solvatomagnetic effect and spin-glass behavior in a 1D coordination polymer constructed from EE-azido bridged Mn^{III}_3O units†

Cai-Ming Liu,* De-Qing Zhang* and Dao-Ben Zhu

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The non-uniform chain manganese(III) complex constructed from EE-azido bridged Mn^{III}_3O units, $[Mn^{III}_3O(Brppz)_3(MeOH)_3(N_3)]\cdot 2MeOH$ [1, Brppz = 3-(5-bromo-2-phenolate)-pyrazolate], is the first example of 1D azido-bridged coordination polymer showing both solvatomagnetic effect and spin-glass behavior.

The magnetic properties of molecular magnets can be modulated by a small change of circumstance, as illustrated by solvatomagnetic effect.[1] Some coordination polymers with such effect have been reported, most of them are high-dimensional porous frameworks displaying long-range magnetic ordering.[1] On the other hand, azido-bridged coordination polymer molecular magnets[2] or single molecular magnets[3] have received increasing attention, however, the study on other magnetic phenomena such as spin-glass behavior in azido-bridged complexes is still lacking.[4] Herein we report the first 1D azido-bridged coordination polymer exhibiting not only a solvatomagnetic effect but also spin-glass behavior, $[Mn^{III}_3O(Brppz)_3(MeOH)_3(N_3)]\cdot 2MeOH$ [**1**, Brppz = 3-(5-bromo-2-phenolate)pyrazolate], which is constructed from EE-azido bridged Mn^{III}_3O cluster units (EE = end-to-end). Interestingly, **1** no longer exhibits spin-glass behavior after losing its crystallized methanol solvent molecules.

1 was obtained from the reaction of Brppz, $Mn(acac)_2$, $Gd(ClO_4)_2\cdot 6H_2O$ and NaN_3 in a methanol–water (10 : 1 v/v) solution.‡ Lanthanide ion is necessary for this reaction[5] though Gd^{3+} is not incorporated into the structure of **1**. Gd^{3+} may abstract $acac^-$ ligand from $Mn(acac)_2$ during reaction. After being exposed to air at room temperature for about two weeks, **1** loses uncoordinated methanol molecules automatically, and the desolvated phase $[Mn^{III}_3O(Brppz)_3(MeOH)_3(N_3)]$ (**2**) was formed. **1** could be recovered easily by recrystallization of **2** using a methanol–water solution. TGA measurement of **2** (which was performed only at low temperature to avoid potential explosion) indicates the coordinated methanol molecules are lost in the range of 40–90 °C, which confirms that **2** is thermally stable in air at room temperature.

X-Ray structural analysis§ reveals that with uncoordinated methanol removal, the general structural motif of the 1D chains remain intact, but the structure undergoes some changes. As shown in Fig. 1 and 2, both **1** and **2** are composed of EE-azido bridged $[Mn^{III}_3O(Brppz)_3(MeOH)_3]^-$ triangular cluster units. The manganese oxidation states were established by bond-valence sum (BVS) calculations[6] and charge balance considerations. The edge of the triangular unit $[Mn^{III}_3(\mu_3\text{-}O^{2-})]$ in both complexes is bridged by the η^1:η^1:μ-pyrazole group of Brppz ligand, whose η^1-phenolate group coordinates to the vertex manganese atom, generating a nearly planar $Mn_3O(N_2O)_3$ moiety. The average intracluster Mn···Mn separation of 3.323 Å in **1** is slightly longer than that in **2** (3.290 Å), and the central oxygen atoms are located 0.1041 and 0.0445 Å above the Mn^{III}_3 planes for **1** and **2**, respectively. Similar properties were also observed in $[Mn^{III}_3O(Meppz)_3(EtOH)_4(OAc)]$ [Meppz = 3-(5-methyl-2-phenolate)pyrazolate],[7a] $[Mn^{III}_3O(Meppz)_3(MeOH)_4(OAc)]$[7b] and $[Mn^{III}_3O(ppz)_3(MeOH)_3(OAc)]$ [ppz = 3-(2-phenolate)pyrazolate] quite recently.[7b] Both Mn1 and Mn3 adopt a distorted octahedral geometry, and possess similar basal planes $[N_2O_2]$, but one azido nitrogen atom and one oxygen atom of methanol molecule occupy the apical positions of Mn1, while two methanol ligands are situated at the two apical positions of Mn3. Differently, Mn2 exhibits a distorted square pyramidal configuration, which shows a similar basal plane $[N_2O_2]$, but an azido nitrogen atom occupying the apical site.

Intermolecular weak interactions play important roles in stabilization of the crystal structures (Fig. S1 and S2, ESI†). The dimer-like double chain structures are formed in both complexes through Mn···Br short contact weak interactions (3.641 and 3.482 Å for **1** and **2**, respectively) between two neighboring 1D chains. The interchain distance separated by the nearest central oxygen atom of the Mn_3O units within the dimer in **1** is 10.141 Å, a little larger than that of **2** (9.823 Å). In addition, within each 1D chain of **1**, there are two types of intermolecular hydrogen bonds among a crystallized methanol solvent molecule and two

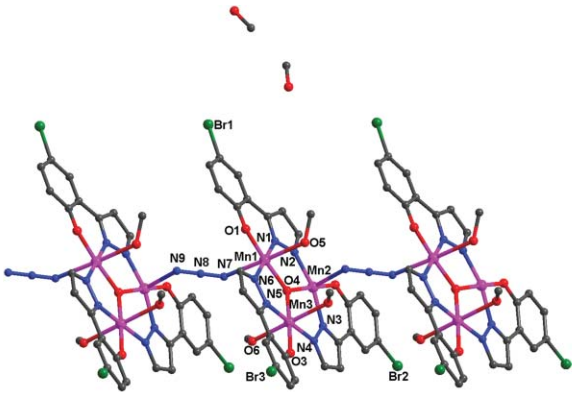

Fig. 1 The 1D chain structure of **1**.

Beijing National Laboratory for Molecular Sciences, Center for Molecular Science, Institute of Chemistry, CAS, Beijing, 100080, P. R. China. E-mail: cmliu@iccas.ac.cn; dqzhang@iccas.ac.cn; Fax: (+86)10-62569349; Tel: (+86)108261-5007

† Electronic supplementary information (ESI) available: The Vogel–Fulcher fit, *M–H* curve and hysteresis loops for **1**. See DOI: 10.1039/b715080f

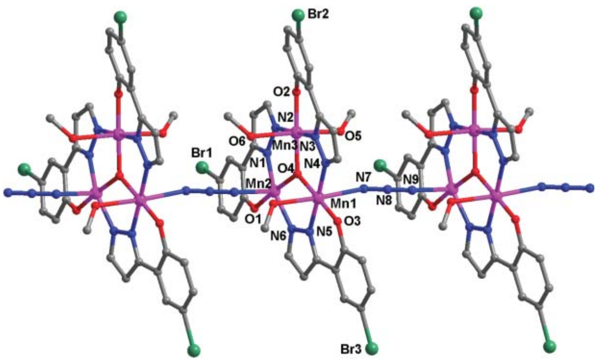

Fig. 2 The 1D chain structure of **2**.

coordinated methanol molecules from two neighboring $[\mathrm{Mn^{III}}_3\mathrm{O(Brppz)_3(MeOH)_3}]^-$ triangular cluster units [$\mathrm{O6^{\#1}\cdots O8}$ 2.795(8) Å and $\mathrm{O7\cdots O8^{\#1}}$ 2.703(9) Å, $^{\#1}$: $-x + 1$, $y - 1/2$, $-z + 1/2$]; while no intermolecular hydrogen bonds exist in **2**. Furthermore, we observed that the coordinated methanol molecules become seriously disordered after desolvation.

The thermal variation χT for **1** and **2** under a 1 kOe applied field in the temperature range of 2–300 K is shown in Fig. 3.¶ The values of χT at room temperature of **1** and **2** are 8.19 and 8.15 emu K mol^{-1}, respectively, somewhat smaller than that expected for three magnetically isolated manganese(III) ions (9.0 emu K mol^{-1} for $g = 2.0$). For **1**, the χT product decreases continuously and falls rapidly when $T < 100$ K upon cooling, reaching a minimum at 24 K. This suggests dominant intracluster antiferromagnetic interactions. Below $T_{\min} = 24$ K, χT increases to a maximum at 7 K, with a value of 25.29 emu K mol^{-1} that is much larger than its room-temperature value, and then falls, which may arise from zero-field splitting, Zeeman effects, and/or weak interchain interactions. For **2**, the χT product decreases continuously from room temperature to 2 K. The great difference of magnetic properties between solvated and desolvated phases at low temperature indicates there is a prominent solvatomagnetic effect for **1**.

The magnetic susceptibility data of **1** and **2** were fitted to the theoretical expression for an isosceles triangle (J_1, J_2) model above 30 K by treating the intrachain interunit interactions with mean-field approximations (zJ),[7a] giving $J_1 = -3.87$ cm^{-1}, $J_2 = -8.20$ cm^{-1}, $g = 2.12$ and $zJ = -0.07$ cm^{-1} with $R = 1.07 \times 10^{-4}$ for **1** and $J_1 = -4.66$ cm^{-1}, $J_2 = -7.35$ cm^{-1}, $g = 2.12$ and $zJ = -0.30$ cm^{-1} with $R = 6.31 \times 10^{-5}$ for **2**. The negative zJ value indicates weak antiferromagnetic interactions *via* EE-azido bridges. The values of J_1/J_2 are 0.47 and 0.63 for **1** and **2**, respectively, which suggests both **1** and **2** have the same ground state ($S = 1$) according to theoretical prediction.[8]

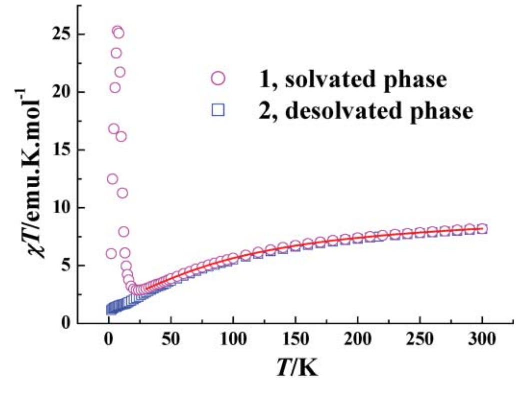

Fig. 3 Plots of χT *vs.* T of **1** and **2** measured under 1 kOe. The solid lines represent the best theoretical fitting.

The divergence of the zero-field cooled (ZFC) and the field cooled (FC) susceptibilities below about 9 K of **1** indicates the occurrence of irreversibility of magnetization (Fig. 4). Both the real χ' and the imaginary χ'' components of the ac susceptibility of **1** show a frequency-dependent peak (Fig. 5). This fact indicates a cooperative freezing of the individual magnetic moments, characteristic of spin-glass, superparamagnet, or single-chain magnet. The shift of peak temperature (T_f) of χ'' is measured by a parameter $\Phi = (\Delta T_\mathrm{f}/T_\mathrm{f})/\Delta(\log \omega)$, where T_f is the freezing temperature and ω is the frequency, giving a Φ value of 0.041, consistent with canonical spin-glass behavior. However, when the ac data were utilized to fit the Arrhenius law, $\tau = \tau_0\exp(\Delta E/k_\mathrm{B})$, no physically realistic values could be obtained (Fig. S3, ESI†), which precludes the occurrence of a superparamagnet, or single-chain magnet.[9] Furthermore, hysteresis can be observed with coercive fields (H_c) of 2 Oe at 4 K, 69 Oe at 3 K and 122 Oe at 2 K, respectively (Fig. S4, ESI†). And the field dependent magnetization of **1** measured at 2 K (Fig. S5, ESI†) shows that at the highest field measured (50 kOe), a very low magnetization value of 1.78 $N\beta$ is achieved and saturation does not occur, this being consistent with weak ferromagnetism owing to spin glass.

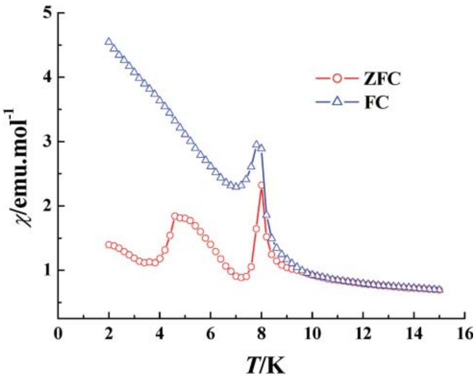

Fig. 4 Plots of FC and ZFC susceptibilities *vs.* temperature of **1** at an applied field of 20 Oe.

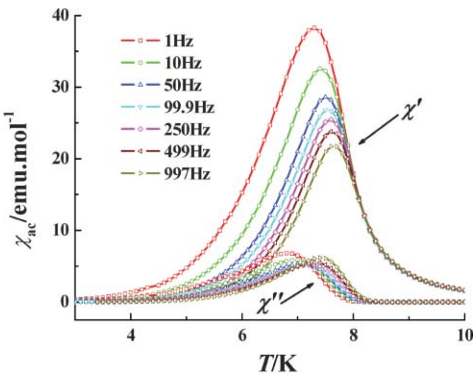

Fig. 5 Ac susceptibilities of **1** measured in an ac field of 1 Oe.

Interestingly, no divergence in the ZFC/FC susceptibility and no peaks in the ac susceptibility of **2** were observed, indicating there is no magnetic phase transition for **2**. It is still not clear why **1** no longer exhibits spin-glass behavior after desolvation. Because the solvated and desolvated phases posses the same spin ground state, the solvatomagnetic effect can not originate from the change of the ground state. We conjecture the intrachain hydrogen bond between the uncoordinated methanol solvent molecule and coordinated methanol molecule plays a critical role in such a spin-glass behavior. It is noteworthy that single molecular magnet behavior and metamagnetic properties have been observed in 1D coordination polymers based on the $Mn^{III}{}_3O$ units recently,[7] while **1** represents the first example of this type of coordination polymer exhibiting spin-glass behavior. Another 1D coordination polymer constructed from mixed molybdenum–vanadium heteropolyoxoanions and nickel(II) complex fragments, $\{[Ni(phen)_2(H_2O)]_2[Ni(phen)_2][V^{IV}{}_8Mo^{VI}{}_6Mo^{V}{}_2O_{40}(PO_4)]\}\{[Ni(phen)_2(H_2O)]_2[V^{IV}{}_8Mo^{VI}{}_6MoV_2O_{40}(PO_4)_2]\}\cdot 5H_2O\cdot 2EtOH$ (phen = 1,10-phenanthroline, EtOH = ethanol) also displays spin-glass behavior at low temperature,[10] but it is an ion-type complex while **1** a neutral one.

In conclusion, the first 1D azido-bridged coordination polymer showing both solvatomagnetic effect and spin-glass behavior has been synthesized and characterized. This work demonstrates that the solvatomagnetic effect can exist in not only high-dimensional open frameworks showing long-range magnetic ordering but also 1D transition metal coordination polymers with spin-glass behavior.

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Notes and references

‡ *Synthesis*: Brppz (0.5 mmol), $Mn(acac)_2$ (0.5 mmol), $Gd(NO_3)_2\cdot 6H_2O$ (0.1 mmol) in 25 mL of methanol–water (10 : 1 v/v) mixed solvents were stirred at room temperature for 10 min, then 0.5 mmol of NaN_3 was added, after stirring for 1 h, a dark green solution was formed, which was allowed to slowly evaporate for about two weeks, giving dark-green block crystals of **1**. Yield: ~30% based on Mn. **2** was obtained by exposing **1** to air at room temperature for two weeks. Elemental analysis (%): calc. for $C_{30}H_{27}Br_3Mn_3N_9O_7$ (**2**): C 34.98, H 2.64, N 12.24; found: C 35.02, H 2.69, N 12.10. IR (KBr): ν = 3423s, 2076m, 1954w, 1550m, 1482s, 1447m, 1398w, 1334w, 1289s, 1247w, 1145m, 1081m, 1018w, 952w, 864w, 812w, 775w, 719m, 664w, 619m, 458w cm^{-1}. **CAUTION:** NaN_3 is potentially explosive and should be handled with care!

§ *Crystal data* for $[Mn^{III}{}_3O(Brppz)_3(MeOH)_3(N_3)]\cdot 2MeOH$ (**1**): monoclinic, $P2_1/c$, a = 19.1576(12), b = 8.2244(5), c = 25.5724(17) Å, β = 98.152(3)°, V = 3988.5(4) Å^3, Z = 4, T = 113(2) K, D_c = 1.821 g cm^{-3}, μ = 4.003 mm^{-1}, GOF = 1.123, $R1$ = 0.0651, $wR2$ = 0.1406 ($I > 2\sigma(I)$). *Crystal data* for $[Mn^{III}{}_3O(Brppz)_3(MeOH)_3(N_3)]$ (**2**): monoclinic, $P2_1/c$, a = 18.476(4), b = 8.138(2), c = 25.446(5) Å, β = 93.25(3)°, V = 3819.8(15) Å^3, Z = 4, T = 293(2) K, D_c = 1.791 g cm^{-3}, μ = 4.170 mm^{-1}, GOF = 0.955, $R1$ = 0.0711, $wR2$ = 0.1456 ($I > \sigma(I)$). Two methyl groups in two coordinated methanol molecules of **2** are disordered, with occupancies of 0.67 and 0.33 for (C28, C29) and (C28′, C29′), respectively. CCDC 662330–662331. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b715080f

¶ The magnetic susceptibility measurements were carried out on numerous fine single crystals (18.88 mg of freshly prepared **1**; after being exposed to air at room temperature for two weeks, it transformed to sample **2**, calc. 17.77 mg) on a Quantum Design MPMS-XL5 SQUID magnetometer. Diamagnetic corrections were estimated from Pascal's constants for all constituent atoms.

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5 Another 1D coordination polymer constructed from $[Mn^{III}{}_3O]$ units, $[Mn^{III}{}_3O(Brppz)_3(MeOH)_3(AcO)]\cdot 0.5MeOH$, was formed without $Ln(ClO_4)_2\cdot 6H_2O$ being utilized, where the acetate anion was possibly generated from the oxidation of $acac^-$ ligand. *Crystal data*: $P2_1/c$, monoclinic, a = 7.604(2), b = 33.436(7), c = 15.726(3) Å, β = 91.95(3)°, V = 3996.0(15) Å^3, Z = 4, T = 293(2) K, D_c = 1.768 g cm^{-3}, μ = 3.992 mm^{-1}, GOF = 1.174, $R1$ = 0.0947, $wR2$ = 0.1878 ($I > 2\sigma(I)$): C. M. Liu *et al.* unpublished work.

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