

## Cyano-Bridged $\text{Mn}^{\text{III}}_3\text{M}^{\text{III}}$ ( $\text{M}^{\text{III}} = \text{Fe}, \text{Cr}$ ) Complexes: Synthesis, Structure, and Magnetic Properties

Hitoshi Miyasaka,<sup>\*,†,‡</sup> Hitomi Takahashi,<sup>†</sup> Tomokura Madanbashi,<sup>†</sup> Ken-ichi Sugiura,<sup>†</sup> Rodolphe Clérac,<sup>\*,§</sup> and Hiroyuki Nojiri<sup>#,‡</sup>

Department of Chemistry, Tokyo Metropolitan University, 1-1 Minami-ohsawa, Hachioji, Tokyo 192-0397, Japan, CREST, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan, Centre de Recherche Paul Pascal, CNRS-UPR 8641, 115 Avenue du Dr. A. Schweitzer, 33600 Pessac, France, and Institute for Materials Research, Tohoku University, Katahira, Aoba, Sendai 980-8577, Japan

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Two cyano-bridged tetranuclear complexes composed of  $\text{Mn}(\text{III})$  salen (salen = *N,N*-ethylene bis(salicylideneiminato)) and hexacyanometalate(III) ( $\text{M} = \text{Fe}, \text{Cr}$ ) in a stoichiometry of 3:1 have been selectively synthesized using  $\{\text{NH}_2(n\text{-C}_{12}\text{H}_{25})_2\}_3[\text{M}^{\text{III}}(\text{CN})_6]$  ( $\text{M}^{\text{III}} = \text{Fe}, \text{Cr}$ ) starting materials:  $[\{\text{Mn}(\text{salen})(\text{EtOH})\}_3\{\text{M}(\text{CN})_6\}]$  ( $\text{M} = \text{Fe}, \mathbf{1}; \text{Cr}, \mathbf{2}$ ). Compounds **1** and **2** are isostructural with a T-shaped structure, in which  $[\text{M}(\text{CN})_6]^{3-}$  assumes a *meridional*-tridentate building block to bind three  $[\text{Mn}(\text{salen})(\text{EtOH})]^+$  units. The strong frequency dependence and observation of hysteresis on the field dependence of the magnetization indicate that **1** is a single-molecule magnet.

Since the beginning of the 1990s, much effort has been directed to the synthesis of cyano-bridged magnetic materials to design classical three-dimensional ordered magnets of Prussian-blue type<sup>1,2</sup> and, more recently, nanosized high-spin complexes exhibiting the so-called single-molecule magnet (SMM) behavior.<sup>3</sup> Since this property is essentially governed

by a high-spin ground state and its anisotropic nature, the assemblies of  $\text{Mn}^{\text{III}}$  salen analogues and polycyanometalate  $[\text{M}^{n+}(\text{CN})_x]^{(n-x)}$  is an interesting strategy to obtain SMM systems. Indeed,  $\text{Mn}^{\text{III}}$  salen complexes possess a strong uniaxial anisotropy induced by the Jahn–Teller distortion of its  $\text{Mn}^{\text{III}}$  metal ions in an octahedral ligand field. Thus, a family of complexes,  $[\{\text{Mn}^{\text{III}}(\text{R-salen})(\text{S})\}_n\{\text{M}^{\text{III}}(\text{CN})_6\}]^{-(3-n)}$  (*R*-salen = salen-type Schiff-base ligand; *S* = a terminal ligand such as  $\text{H}_2\text{O}$  or alcohols;  $\text{M}^{\text{III}} = \text{Fe}, \text{Cr}$ ), has been synthesized so far, but only a few compounds have been structurally characterized<sup>4</sup> with  $n = 1$ :  $(\text{NEt}_4)_2[\text{Mn}(\text{saldmen})(\text{H}_2\text{O})][\text{Fe}(\text{CN})_6]$  (saldmen<sup>2-</sup> = *N,N*-(1,1-dimethylethylene)-bis(salicylideneiminato) dianion);<sup>5</sup> with  $n = 2$ :  $\text{K}[\text{Mn}(5\text{-Rsalen})_2][\text{M}(\text{CN})_6]$  ( $\text{M} = \text{Fe}, \text{Cr}$ ),<sup>6,7</sup> and  $(\text{NEt}_4)[\text{Mn}(\text{salmen})(\text{EtOH})_2][\text{Fe}(\text{CN})_6]$  (salmen<sup>2-</sup> = *N,N*-(1-methylethylene)bis(salicylideneiminato) dianion);<sup>5</sup> and with  $n = 6$ :  $\{[\text{Mn}(\text{salen})(\text{H}_2\text{O})]_6[\text{M}(\text{CN})_6]\}_3\{\text{M}(\text{CN})_6\}$  ( $\text{M} = \text{Fe}, \text{Cr}$ ) (salen<sup>2-</sup> = *N,N*-ethylenebis(salicylideneiminato) dianion).<sup>8,9</sup> Interestingly, among these complexes, those with  $n = 2$  possess SMM behavior.<sup>7,10</sup> Herein, we report on the synthesis, crystal structure, and magnetic properties of new  $n = 3$  complexes: <sup>11</sup>  $[\text{Mn}(\text{salen})(\text{EtOH})]_3[\text{M}(\text{CN})_6] \cdot \text{solvents}$  ( $\text{M} = \text{Fe}, \mathbf{1} \cdot 2\text{MeOH} \cdot 2\text{H}_2\text{O}; \text{Cr}, \mathbf{2} \cdot 2\text{MeOH} \cdot \text{H}_2\text{O}$ ).

\* To whom correspondence should be addressed. E-mail: miyasaka@comp.metro-u.ac.jp (H.M.).

<sup>†</sup> Tokyo Metropolitan University.

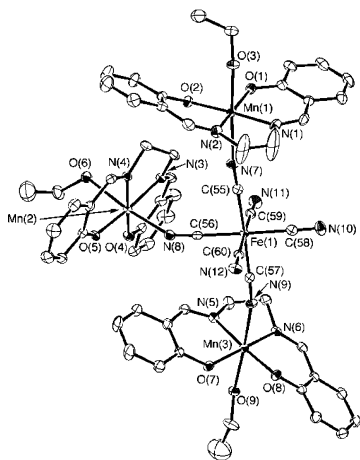
<sup>‡</sup> CREST, JST.

<sup>§</sup> Centre de Recherche Paul Pascal.

<sup>#</sup> Institute for Materials Research.

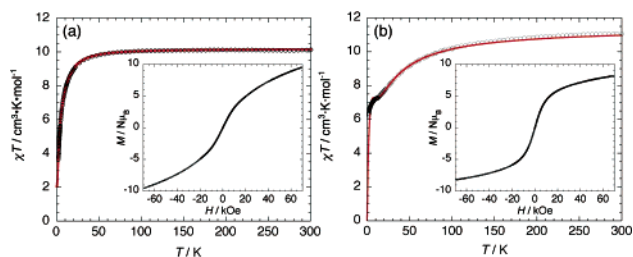
- (1) For example: (a) Mallah, T.; Thiébaud, S.; Verdagner, M.; Veillet, P. *Science* **1993**, *262*, 1554. (b) Entley, W. R.; Girolami, G. S. *Inorg. Chem.* **1994**, *33*, 5165, and its correction **1995**, *34*, 2262. (c) Entley, W. R.; Girolami, G. S. *Science* **1995**, *268*, 397. (d) Ferlay, S.; Mallah, T.; Ouahés, R.; Veillet, P.; Verdagner, M. *Nature* **1995**, *378*, 701. (e) Sato, O.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *Science* **1996**, *272*, 704. (f) Dujardin, E.; Ferlay, S.; Phan, X.; Desplanches, C.; Cartier dit Moulin, C.; Sainctavit, P.; Baudelet, F.; Dartyge, E.; Villet, P.; Verdagner, M. *J. Am. Chem. Soc.* **1998**, *120*, 11347. (g) Garde, R.; Villain, F.; Verdagner, M. *J. Am. Chem. Soc.* **2002**, *124*, 10531. (h) Franz, P.; Ambrus, C.; Hauser, A.; Cgernyshov, D.; Hostettler, M.; Hauser, J.; Keller, L.; Krämer, K.; Stoeckli-Evans, H.; Pattison, P.; Bürgi, H.-B.; Decurtins, S. *J. Am. Chem. Soc.* **2004**, *126*, 16472. (i) Dong, W.; Zhu, L.; Song, H.; Liao, D.; Jiang, Z.; Yan, S.; Cheng, P.; Gao, S. *Inorg. Chem.* **2004**, *43*, 2465. (j) Ohkoshi, S.; Matsuda, T.; Tokoro, H.; Hashimoto, K. *Chem. Mater.* **2005**, *17*, 81.
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- (4) The compound with  $n = 4$  has been reported as  $[\text{Mn}(\text{saltmen})(\text{EtOH})]_4[\text{Fe}(\text{CN})_6]\text{ClO}_4$  (saltmen<sup>2-</sup> = *N,N*-(1,1,2,2-tetramethylethylene) bis(salicylideneiminato) dianion), but no structural characterization has been given. See ref 5.
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**Figure 1.** ORTEP drawing of **1** (50% probability ellipsoid).

Compounds **1** and **2** were synthesized by the assembly reactions of  $[\text{Mn}(\text{salen})(\text{H}_2\text{O})]\text{ClO}_4$  with  $\{\text{NH}_2(n\text{-C}_{12}\text{H}_{25})_2\}_3^-$   $[\text{M}(\text{CN})_6]$  ( $\text{M} = \text{Fe}, \text{Cr}$ ) in a 1:1 mixing ratio in a MeOH/EtOH solution (>60% yield for both compounds).<sup>12</sup> Despite the reaction in the mixing ratio of 1:1, the stoichiometry of the final compounds is unambiguously 3:1, forming a class of neutral complexes. It is worth noticing that the use of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  in a MeOH/H<sub>2</sub>O medium instead of  $\{\text{NH}_2(n\text{-C}_{12}\text{H}_{25})_2\}_3[\text{Fe}(\text{CN})_6]$  led to a compound with the same 3:1 stoichiometry but including several oligomeric species in its crystal structure.<sup>6</sup> Compounds **1** and **2** crystallize in the same monoclinic space group  $P2_1/c$  and are isostructural with similar unit-cell dimensions.<sup>13</sup> An ORTEP drawing of **1** is depicted in Figure 1 (Figure S1 for **2**). (CIF files are also available on application to the Cambridge Data Centre, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk): CCDC-268707 for **1** and 268708 for **2**.) In both compounds, the  $\text{M}(\text{CN})_6$  moiety acts as a meridional- $\mu_3$ -coordinating-donor building-block and binds three  $\text{Mn}(\text{salen})(\text{EtOH})$  moieties.  $\text{Mn}-\text{N}_{\text{CN}}$  bond distances are very similar, ranging from 2.249(2) to 2.307(2) Å for **1** and from 2.234(4) to 2.293(4) Å for **2**, but significantly different  $\text{Mn}-\text{N}-\text{C}$  angles are found with  $\text{Mn}(1)-\text{N}(7)-\text{C}(55) = 170.7(2)^\circ$ ,  $168.7(4)^\circ$ ,  $\text{Mn}(2)-\text{N}(8)-\text{C}(56) = 148.9(2)^\circ$ ,  $149.9(4)^\circ$ , and  $\text{Mn}(3)-\text{N}(9)-\text{C}(57) =$



**Figure 2.**  $\chi T$  vs  $T$  plots of **1** (a) and **2** (b) at 1000 Oe. The solid red lines are simulated curves based on a Heisenberg tetranuclear model (see text). Insets:  $M$  vs  $H$  plots of **1** (a) and **2** (b) at 1.8 K.

$161.9(2)^\circ$ ,  $161.5(4)^\circ$ , for **1** and **2**, respectively. Each  $\text{Mn}(\text{salen})(\text{EtOH})$  moiety has an elongated octahedral geometry with a Jahn–Teller distortion along the  $(\text{EtOH})-\text{Mn}-\text{N}_{\text{CN}}$  axis ( $\text{Mn}-\text{O}_{\text{EtOH}}$  ranges from 2.307(2) to 2.360(2) Å for **1** and from 2.290(3) to 2.325(3) Å for **2**). Equatorial  $\text{Mn}-\text{X}$  ( $\text{X} = \text{N}$  and  $\text{O}$ ) bond distances are typically found below 2 Å.

Figure 2 shows plots of  $\chi T$  vs  $T$  for **1** and **2** measured in the temperature range 1.8–300 K at 1000 Oe. Above 50 K, the susceptibility obeys the Curie–Weiss law with  $C = 10.3 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$  and  $\theta = -2.4 \text{ K}$  for **1** and  $C = 11.6 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$  and  $\theta = -13.7 \text{ K}$  for **2**, respectively. For **1**, the  $\chi T$  product is almost independent of temperature in the 100–300 K range ( $10.13 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ ) and then gradually and continuously decreases to 1.8 K ( $3.66 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ ). To evaluate exchange couplings between  $\text{Mn}^{\text{III}}$  ( $S_{\text{Mn}} = 2$ ) ion and  $\text{Fe}^{\text{III}}$  ion ( $S_{\text{Fe}} = 1/2$ ) via an  $-\text{NC}-$  bridge, the magnetic susceptibility was simulated using a Heisenberg four-spin model (centered-triangle model) Hamiltonian:<sup>14</sup>

$$H = -2J_1(S_{\text{Mn}1} \cdot S_{\text{M}}) - 2J_2(S_{\text{Mn}2} \cdot S_{\text{M}}) - 2J_3(S_{\text{Mn}3} \cdot S_{\text{M}}) \quad (1)$$

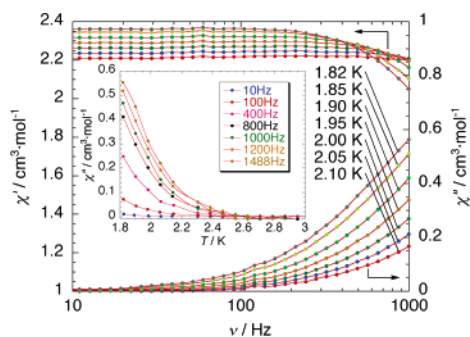
where  $S_{\text{M}} = S_{\text{Fe}}$  and  $J_1$ ,  $J_2$ , and  $J_3$  are  $\text{Mn} \cdots \text{Fe}$  interactions. As the three  $\text{Mn}-\text{NC}-\text{Fe}$  bridges are structurally independent, these couplings are indeed expected to be different ( $J_1 \neq J_2 \neq J_3$ ). Nevertheless, simulation of the experimental data was performed step-by-step. First, the three interactions have been identically treated, but no satisfactory solution has been found. Therefore, the second step was performed for a case in which two interactions are maintained in equal and the third one is free (note that  $\text{Mn}1-\text{NC}-\text{Fe}$  and  $\text{Mn}3-\text{NC}-\text{Fe}$  bridges are similar structurally speaking, and hence,  $J_1$  and  $J_3$  should not be much different). With this approach, the experimental data were well simulated down to 2 K with  $g_{\text{av}} = 2.085(2)$ ,  $J_1/k_{\text{B}} = J_3/k_{\text{B}} = -4.0(1) \text{ K}$ , and  $J_2/k_{\text{B}} = +4.8(1) \text{ K}$  for **1** (solid red line in Figure 2a). No improvement of the fitting was obtained using three independent  $J$  parameters. Two of three  $\text{Mn} \cdots \text{Fe}$  exchanges are thus antiferromagnetic, whereas the last one is, indeed, necessarily ferromagnetic to simulate correctly the experimental results. In addition, the magnitude of exchange couplings falls, for both ferromagnetic and antiferromagnetic ones, in the range of values reported previously.<sup>5,7,8,9b–11</sup> Empirically,  $\text{Mn}-\text{N}-\text{C}$  bond

(11) Marvilliers et al. have reported an example of cyano-bridged  $\text{Mn}^{\text{III}}_3\text{-Cr}$  using a pentadentate ligand. However, no crystal structure has been reported in the literature. Marvilliers, A.; Mallah, T.; Riviere, E.; Parsons, S.; Munoz, C.; Vostrikova, K. E. *Mol. Cryst. Liq. Cryst.* **1999**, *335*, 483.

(12) Anal. Calcd for  $1 \cdot 2\text{H}_2\text{O} \cdot 2\text{MeOH}$  (%): C, 52.67; H, 5.13; N, 11.89. Found: C, 52.90; H, 4.55; N, 12.39. IR (KBr pellet):  $\nu(\text{C}\equiv\text{N})$ , 2118  $\text{cm}^{-1}$ ;  $\nu(\text{C}=\text{N})$ , 1601, 1624  $\text{cm}^{-1}$ . Anal. Calcd for  $2 \cdot \text{H}_2\text{O} \cdot 3\text{MeOH}$  (%): C, 53.13; H, 5.24; N, 11.80. Found: C, 52.88; H, 4.97; N, 11.92. IR (KBr pellet):  $\nu(\text{C}\equiv\text{N})$ , 2131  $\text{cm}^{-1}$ ;  $\nu(\text{C}=\text{N})$ , 1601, 1624  $\text{cm}^{-1}$ .

(13) Crystal data for **1**:  $\text{C}_{62}\text{H}_{72}\text{N}_{12}\text{O}_{13}\text{Mn}_3\text{Fe}$ , fw = 1413.98, monoclinic  $P2_1/n$  (#14),  $T = -180 \pm 1^\circ \text{C}$ ,  $a = 15.772(2) \text{ \AA}$ ,  $b = 14.454(2) \text{ \AA}$ ,  $c = 29.129(4) \text{ \AA}$ ,  $\beta = 104.240(2)^\circ$ ,  $V = 6436.5(14) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_{\text{calc}} = 1.459 \text{ g} \cdot \text{cm}^{-3}$ ,  $F_{000} = 2932.00$ ,  $\mu(\text{Mo K}\alpha) = 8.67 \text{ cm}^{-1}$ , Final R1 = 0.041 ( $I > 2.00\sigma(I)$ ), R = 0.052 (all data) wR2 = 0.131 (all data), GOF = 1.003,  $\rho_{\text{max}} = 1.48 \text{ e}^-/\text{\AA}^3$ ,  $\rho_{\text{min}} = -0.99 \text{ e}^-/\text{\AA}^3$ . Crystal data for **2**:  $\text{C}_{62}\text{H}_{70}\text{N}_{12}\text{O}_{12}\text{Mn}_3\text{Cr}$ , fw = 1392.12, monoclinic  $P2_1/n$  (#14),  $T = -180 \pm 1^\circ \text{C}$ ,  $a = 15.8314(13) \text{ \AA}$ ,  $b = 14.5301(11) \text{ \AA}$ ,  $c = 29.226(2) \text{ \AA}$ ,  $\beta = 104.9231(13)^\circ$ ,  $V = 6496.1(9) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_{\text{calc}} = 1.423 \text{ g} \cdot \text{cm}^{-3}$ ,  $F_{000} = 2884.00$ ,  $\mu(\text{Mo K}\alpha) = 8.02 \text{ cm}^{-1}$ , Final R1 = 0.064 ( $I > 2.00\sigma(I)$ ), R = 0.081 (all data) wR2 = 0.150 (all data), GOF = 1.246,  $\rho_{\text{max}} = 2.32 \text{ e}^-/\text{\AA}^3$ ,  $\rho_{\text{min}} = -1.02 \text{ e}^-/\text{\AA}^3$ .

(14) The susceptibility was calculated using the MAGPACK package developed by J. M. Clemente-Juan et al. Borrás-Almenar, J. J.; Clemente-Juan, J. M.; Coronado, E.; Tsukerblat, B. S. *J. Comput. Chem.* **2001**, *22*, 985.

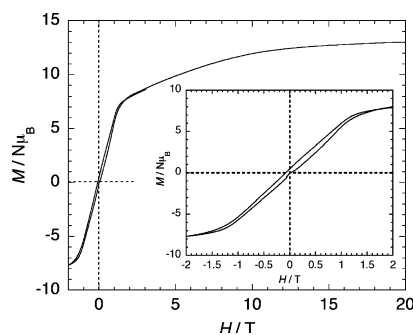


**Figure 3.** Frequency and temperature dependence of ac susceptibilities ( $\chi'$ , in-phase;  $\chi''$ , out-of-phase) of **1** (zero dc field and 3 Oe ac field).

angles close to  $150^\circ$  tend to favor ferromagnetic coupling in cyano-bridged  $\text{Mn}^{\text{III}}-\text{Fe}^{\text{III}}$  systems.<sup>7,8,9b,10</sup> Therefore, the  $\text{Mn}(2)-\text{N}(8)-\text{C}(56)$  link with a  $149^\circ$  angle could mediate ferromagnetic exchange, while  $\text{Mn}(1)-\text{N}(7)-\text{C}(55)$  and  $\text{Mn}(3)-\text{N}(9)-\text{C}(57)$  possessing larger angles ( $>161^\circ$ ) would stabilize antiferromagnetic interactions. Consequently, this coupling scheme leads to an  $S_{\text{T}} = 3/2$  spin ground state in agreement with the  $\chi'T$  value observed at low temperature ( $\chi'$ : in-phase ac susceptibility) (Figure S2). It should be noted that, in addition to the intracomplex exchange interactions, contributions from the anisotropy of  $\text{Mn}^{\text{III}}$  ions ( $D$ ) and intercomplex antiferromagnetic interactions ( $zJ$ ) are probably relevant below 5 K. Therefore, the obtained  $J$  values may be slightly overestimated.

The  $\chi T$  product of **2** decreases gradually from 300 K ( $11.1 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ ) then reaches a plateau at about 20 K and finally decreases again below 10 K ( $7.2 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$  at 10 K,  $6.2 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$  at 1.8 K). The magnetic susceptibility was calculated<sup>14</sup> using the Hamiltonian given in eq 1 with  $S_{\text{M}} = S_{\text{Cr}}$ . The treatment with equal  $J$  values led to a very good fit, which was slightly improved introducing the intercomplex interaction in mean-field approximation ( $zJ'$ ):<sup>15,16</sup>  $g_{\text{av}} = 2.03(1)$ ,  $J_1/k_{\text{B}} = J_2/k_{\text{B}} = J_3/k_{\text{B}} = -2.3(1) \text{ K}$ ,  $zJ'/k_{\text{B}} = -0.2(1) \text{ K}$  for **2** (solid red line in Figure 2b). This coupling scheme leads to an  $S_{\text{T}} = 9/2$  spin ground state confirmed by the  $M$  vs.  $H$  plot at 1.8 K (inset Figure 2b) which is almost saturated at 7 T reaching  $8.3 \mu_{\text{B}}$ . The estimation of the exchange coupling between  $\text{Mn}^{\text{III}}$  and  $\text{Cr}^{\text{III}}$  ions via the  $-\text{NC}-$  linkage agrees well with literature values ranging from  $-1.6$  to  $-3.6 \text{ K}$ ,<sup>7,9,11</sup> always found of antiferromagnetic nature. Nevertheless, the obtained  $J$  value must be taken with some caution, taking into account the adopted approximations (i) the three nonequivalent  $\text{Mn} \cdots \text{Cr}$  interactions being equally treated and (ii) the anisotropic effects being neglected.

To probe the dynamics of the magnetization for **1** and **2**, ac susceptibility was measured at an oscillating ac field of 3 Oe as a function of frequency (1–1488 Hz) and temperature (1.8–4 K). Reliable and reproducible ac signals were detected only for **1** (Figure 3). Below 2.1 K, the increase of



**Figure 4.**  $M$  vs  $H$  data measured on a polycrystalline sample of **1** at 0.5 K. Inset: Magnification of the  $M$  vs  $H$  plot at low fields between  $-2$  and  $2 \text{ T}$ .

out-of-phase ac susceptibility ( $\chi''$ ) observed above 100 Hz and its temperature dependence clearly indicate the presence of magnetization relaxation. Since the  $\chi'T$  vs  $T$  plot is still decreasing even at low temperatures without a clear plateau (Figure S2), low-lying excited states are thus thermally populated even at 1.8 K (energy diagrams of **1** and **2**, calculated using susceptibility-fitting parameters, are given in Figure S3). This conclusion is also supported by the field dependence of the magnetization for **1** at 1.8 K, which reaches values (ca.  $9.5 \mu_{\text{B}}$  at 7 T) larger than  $3 \mu_{\text{B}}$  expected for the  $S_{\text{T}} = 3/2$  ground state (inset of Figure 1 and Figure S4). Despite the presence of low-lying excited states and a small  $S_{\text{T}}$  value, ac susceptibility measurements strongly suggest that **1** is a SMM.

To confirm this hypothesis, field dependence of the magnetization has been measured on a polycrystalline sample of **1** at 0.5 K and external fields up to 20 T. Figure 4 shows these data and revealed a hysteresis behavior expected for a SMM. It is worth noting that the magnetization reaches a clear saturation of  $13 \mu_{\text{B}}$  expected for the highest spin state ( $S_{\text{T}} = 13/2$ ) available for **1**. This result demonstrates that all the spin levels can be explored with fields up to 20 T and further confirms the presence of low-lying excited states.

In summary, a new family of cyano-bridged  $\text{Mn}^{\text{III}}_3\text{M}^{\text{III}}$  ( $\text{M}^{\text{III}} = \text{Fe}, \text{Cr}$ ) tetranuclear complexes,  $[\{\text{Mn}(\text{salen})(\text{EtOH})\}_3\text{-}\{\text{M}(\text{CN})_6\}]$  ( $\text{M} = \text{Fe}, \mathbf{1}; \text{Cr}, \mathbf{2}$ ), has been selectively synthesized using  $\{\text{NH}_2(n\text{-C}_{12}\text{H}_{25})_2\}_3[\text{M}^{\text{III}}(\text{CN})_6]$  as a starting material. The effective exchange couplings between  $\text{Mn}^{\text{III}}$  and  $\text{M}^{\text{III}}$  ions afford a spin ground state of  $S_{\text{T}} = 3/2$  for **1** and  $S_{\text{T}} = 9/2$  for **2**, respectively. Despite a small  $S_{\text{T}}$  value and the presence of low-lying excited spin states, **1** exhibits characteristic features of SMM behavior.

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**Supporting Information Available:** X-ray crystallographic files of **1** and **2** in CIF format and Figures S1–S4. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(16) It should be noted that ZFS effects from  $\text{Mn}^{\text{III}}$  ions have been considered instead of intercomplex interaction in an alternative model, but no acceptable fitting of the data has been obtained.