Inorg. Chem. **2006**, *45*, 4877–4879

Inorganic Chemistry
Communication

One-Dimensional Ferromagnetic Complexes Built with Mn^{III}_3O Units

Jun Tao,[†,‡] Yuan-Zhu Zhang,[‡] Yue-Lin Bai,[†] and Osamu Sato*[,‡]

Department of Chemistry, Xiamen University, Xiamen 361005, People's Republic of China, and Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga, 816-8580 Fukuoka, Japan

Received January 27, 2006

Two chain complexes built with non-carboxylate Mn^{III}_3O units, $[Mn_3O(ppz)_3(MeOH)_3(OAc)]_n$ (**1**) and $[Mn_3O(Meppz)_3(MeOH)_4(OAc)]_n$ (**2**), were synthesized and characterized. Magnetic studies revealed similar intrachain ferromagnetic interactions in them and field-induced metamagnetic properties in **1**.

Recent progress in single-molecule magnets[1] and single-chain magnets[2] has renewedly brought much attention to the low-dimensional molecule-based magnetic materials, which have long since provided practical examples for understanding fundamental phenomena in magnetism and for testing models that cannot be elucidated in higher dimensions.[3] As for one-dimensional magnetic materials, though great efforts have been made on them, it is still a great challenge to predict and control bulk magnetic properties through tuning of the nature and magnitude of intrachain couplings and/or interchain interactions. One promising way to meet the demand may be the assembly reaction of metalloclusters with unambiguous magnetic properties and bridges with known superexchange character. This strategy has been recently used to synthesize several one-dimensional materials with interesting magnetic properties.[4] In our efforts to explore new one-dimensional magnetic materials, we notice that the oxo-centered manganese cluster, $\{Mn_3O(O_2CR)_6(L)_3\}^{0/+}$, has been studied in great detail[5] and proven to be a feasible building unit to form one-dimensional complexes.[6] Here we report two complexes constructed from non-carboxylate Mn^{III}_3O clusters of in situ generation for the first time, $[Mn^{III}_3O(ppz)_3(MeOH)_3(OAc)]_n$ (**1**) and $[Mn^{III}_3O(Meppz)_3(MeOH)_4(OAc)]_n$ (**2**) [H_2ppz = 3-(2-hydroxyphenyl)pyrazole and H_2Meppz = 3-(2-hydroxy-5-methylphenyl)pyrazole], respectively. The formation of planar $Mn^{III}_3O(ppz)_3$ or $Mn^{III}_3O(Meppz)_3$ moieties makes it possible to link them via bridges at the Mn^{III} axial positions to form one-dimensional complexes, and the magnetic properties can thus be controlled by the introduction of selected bridges.

A methanol solution (15 mL) containing H_2ppz (or H_2Meppz, 0.1 mmol), $NaOCH_3$ (0.2 mmol), and $Mn(OAc)_2 \cdot 4H_2O$ (0.1 mmol) was stirred for 30 min and filtered, and the dark-green filtrate was left for slow evaporation to give dark-celadon platelike crystals of **1** (or **2**).

X-ray structure analysis[7] shows that both **1** and **2** possess a near-equilateral Mn^{III}_3O triangular building unit, whose

---

* To whom correspondence should be addressed. E-mail: sato@cm.kyushu-u.ac.jp.

[†] Xiamen University.

[‡] Kyushu University.

(1) (a) Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. *Nature* **1993**, *365*, 141. (b) Sessoli, R.; Tsai, H. L.; Schake, A. R.; Wang, S.; Vincent, J. B.; Folting, K.; Gatteschi, D.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 1804. (c) Ruiz, D.; Sun, Z.; Albela, B.; Folting, K.; Christou, G.; Hendrickson, D. N. *Angew. Chem., Int. Ed.* **1998**, *37*, 300. (d) Wernsdorfer, W.; Aliaga-Alcalde, N.; Hendrickson, D. N.; Christou, G. *Nature* **2002**, *416*, 406. (e) Gatteschi, D.; Sessoli, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 268. (f) Oshio, H.; Hoshino, N.; Ito, T.; Nakano, M. *J. Am. Chem. Soc.* **2004**, *126*, 8805. (g) Brechin, E. K. *Chem. Commun.* **2005**, 5141. (h) Stamatatos, T. C.; Foguet-Albiol, D.; Stoumpos, C. C.; Raptopoulou, C. P.; Terzis, A.; Wernsdorfer, W.; Perlepes, S. P.; Christou, G. *J. Am. Chem. Soc.* **2005**, *127*, 15380. (i) Ni, Z.-H.; Kou, H.-Z.; Zhang, L.-F.; Ge, C.; Cui, A.-L.; Wang, R.-J.; Li, Y.-D.; Sato, O. *Angew. Chem., Int. Ed.* **2005**, *44*, 7742.

(2) (a) Caneschi, A.; Gatteschi, D.; Lalioti, N.; Sangregorio, C.; Sessoli, R.; Venturi, G.; Vindigni, A.; Rettori, A.; Pini, M. G.; Novak, M. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 1760. (b) Clérac, R.; Miyasaka, H.; Yamashita, M.; Coulon, C. J. *J. Am. Chem. Soc.* **2002**, *124*, 12837. (c) Liu, T. F.; Fu, D.; Gao, S.; Zhang, Y. Z.; Sun, H. L.; Su, G.; Liu, Y. J. *J. Am. Chem. Soc.* **2003**, *125*, 13976. (d) Pardo, E.; Ruiz-García, R.; Lloret, F.; Faus, J.; Julve, M.; Journaux, Y.; Delgado, F.; Ruiz-Pérez, C. *Adv. Mater.* **2004**, *16*, 1597. (e) Kajiwara, T.; Nakano, M.; Kaneko, Y.; Takaishi, S.; Ito, T.; Yamashita, M.; Igashira-Kamiyama, A.; Nojiri, H.; Ono, Y.; Kojima, N. *J. Am. Chem. Soc.* **2005**, *127*, 10150.

(3) (a) Kahn, O. *Molecular Magnetism*; VCH: New York, 1993. (b) De Jongh, L. J. *Adv. Phys.* **1974**, *23*, 1. (c) Miller, J. S., Drilon, M., Eds. *Manetism: Molecules to Materials*; Wiley-VCH: Weinheim, Germany, 2002.

(4) (a) Chakov, N. E.; Wernsdorfer, W.; Abboud, K. A.; Christou, G. *Inorg. Chem.* **2004**, *43*, 5919. (b) Miyasaka, H.; Nezu, T.; Sugimoto, K.; Sugiara, K.; Yamashita, M.; Clérac, R. *Chem.—Eur. J.* **2005**, *11*, 1592. (c) Ferbinteanu, M.; Miyasaka, M.; Wernsdorfer, W.; Nakata, K.; Sugiura, K.; Yamashita, M.; Coulon, C.; Clérac, R. *J. Am. Chem. Soc.* **2005**, *127*, 390. (d) Joo, Y.; Wernsdorfer, W.; Yang, E.-C.; Nakano, M.; Rheingold, A. L.; Hendrickson, D. N. *Inorg. Chem.* **2005**, *44*, 3377. (e) Lecren, L.; Roubeau, O.; Coulon, C.; Li, Y.-G.; Le Goff, X. F.; Wernsdorfer, W.; Miyasaka, H.; Clérac, R. *J. Am. Chem. Soc.* **2005**, *127*, 17353.

(5) (a) Baikie, A. R. E.; Hursthouse, M. B.; New, D. B.; Thornton, P. *J. Chem. Soc., Chem. Commun.* **1978**, 62. (b) Vincent, J. B.; Chang, H. R.; Folting, K.; Huffman, J. C.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1987**, *109*, 5703. (c) McCusker, J. K.; Jang, H. G.; Wang, S.; Christou, G.; Hendrickson, D. N. *Inorg. Chem.* **1992**, *31*, 1874. (d) Wu, R.; Poyraz, M.; Sowrey, F. E.; Anson, C. E.; Wocaldo, S.; Powell, A. K.; Jayasooriya, U. A.; Cannon, R. D.; Nakanoto, T.; Katada, M.; Sano, H. *Inorg. Chem.* **1998**, *37*, 1913. (e) Li, J.; Yang, S.-M.; Zhang, F.-X.; Tang, Z.-X.; Ma, S.-L.; Shi, Q.-Z.; Wu, Q.-J.; Huang, Z.-X. *Inorg. Chem. Acta* **1999**, *294*, 109. (f) Zhang, S. W.; Wei, Y. G.; Liu, Q.; Shao, M. C.; Zhou, W. S. *Polyhedron* **1996**, *15*, 1041.

(6) Kim, J.; Lim, J. M.; Do, Y. *Eur. J. Inorg. Chem.* **2003**, 2563.

10.1021/ic060159y CCC: $33.50

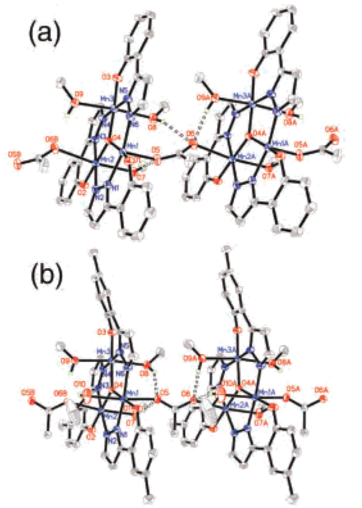


Figure 1. One-dimensional structures of **1** (a) and **2** (b) showing the Mn^{III}_3O building units with labels and the intrachain hydrogen bonds. Symmetry codes: (A) x, $y-1$, z and (B) x, $y+1$, z for **1**; (A) $x+1$, y, z and (B) $x-1$, y, z for **2**.

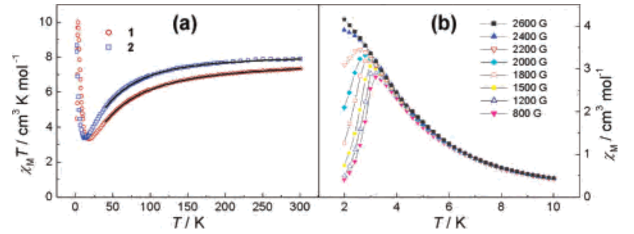


Figure 2. (a) Magnetic susceptibilities of **1** and **2** under applied fields of 2 kG (**1**) and 1 kG (**2**), respectively. (b) Temperature dependence of the FCM at various fields for **1**.

edges are bridged by ppz^{2-} (**1**) and $Meppz^{2-}$ (**2**) with average intracluster Mn···Mn separations of 3.295 and 3.306 Å for **1** and **2**, respectively (Figure 1), and the central μ_3-O^{2-} ions locate 0.110 Å (for **1**) and 0.015 Å (for **2**) above the Mn^{III}_3 planes. The Mn^{III} oxidation states in **1** and **2** were established by bond valence sum (BVS) calculations,[8] charge balance considerations, and the observed Mn^{III} Jahn−Teller distortion. For **1** (Figure 1a), the three Mn^{III} ions in the building unit locate in similar basal planes, which are composed of the central μ_3-O^{2-} ion, one nitrogen atom, and one phenolate oxygen atom from one ppz^{2-} ligand and one nitrogen atom from another one. The differences of coordination geometries in them consist of coordination atoms in their apical positions; those are an acetate oxygen atom (O5) for Mn1, a methanol oxygen atom (O7) and an acetate oxygen atom (O6B) for Mn2, and methanol oxygen atoms (O8 and O9) for Mn3. For **2** (Figure 1b), all three Mn^{III} ions lie in coordination geometries similar to those for complex **1** except that Mn1 in **2** is six-coordinated with the apical positions occupied by an acetate oxygen atom (O5) and a methanol oxygen atom (O10).

Each ppz^{2-}- or $Meppz^{2-}$-bridged Mn^{III}_3O cluster is then connected to adjacent ones via *n*-glide operations by using acetate groups as bridges in an anti−anti conformation to form stepwise chains for **1** and **2**, respectively. The acetato-bridged Mn···Mn distance in **1** (6.39 Å) is a little shorter than that in **2** (6.58 Å). It should be noticed that the chains are stabilized not only by covalent bonds between Mn^{III} ions and acetate groups but also by hydrogen bonds between oxygen atoms of acetate groups and coordinated methanol molecules, i.e., three hydrogen bonds of O7−H···O5 [2.851(3) Å], O8−H···O6 [2.997(3) Å], and O9A−H···O6 [2.839(3) Å] in **1** and four hydrogen bonds of O7−H···O5 [2.913(4) Å], O8−H···O5 [2.692(4) Å], O9A−H···O6 [2.658(4) Å], and O10A−H···O6 [3.224(5) Å] in **2** (Figure 1), respectively. The stacking modes of **1** and **2** are quite different in such way that $Mn^{III}_3O(ppz)_3$ moieties in **1** arranged in a herringbone style while $Mn^{III}_3O(Meppz)_3$ moieties in **2** ranked parallel (Figure S1in the Supporting Information), giving shortest interchain Mn···Mn distances of 7.341 and 8.359 Å for **1** and **2**, respectively. These differences obviously arise from the different steric hindrances of ppz^{2-} and $Meppz^{2-}$.

The magnetic susceptibilities of **1** and **2** (per Mn^{III}_3 unit) were measured under fields of 2 kG (for **1**) and 1 kG (for **2**) in the 2−300 K temperature range. The $\chi_M T$ values are 7.34 and 7.89 cm^3 K mol^{-1} for **1** and **2** at room temperature (Figure 2a), respectively, somewhat less than the spin-only one (9.0 cm^3 K mol^{-1}) expected for three isolated Mn^{III} ions. Upon cooling, the $\chi_M T$ products generally decrease in the high-temperature range and rapidly at $T < 100$ K and then reach a minimum at 18 and 9 K for **1** and **2**, respectively. The data of χ_M^{-1} above 100 K fit well with the Curie−Weiss law, giving $C = 8.1$ cm^3 K mol^{-1} and $\theta = -30.6$ K for **1** and $C = 8.5$ cm^3 K mol^{-1} and $\theta = -21.5$ K for **2** (Figure S3 in the Supporting Information), respectively. The Curie constants are in good agreement with three uncoupled Mn^{III} ions with average g values of 1.90 and 1.92 for **1** and **2**, respectively. The negative Weiss constants indicate that the intracluster interactions in **1** and **2** are antiferromagnetic (AF), in accord with the magnetic properties of known planar Mn^{III}_3O clusters.[5b,e] On lowering temperatures, $\chi_M T$ sharply increases, suggesting a ferrimagnetic-like character, which could be explained as the noncompensated spin-frustrated Mn^{III}_3O clusters being further ferromagnetically coupled through the acetate bridges. The further sharp decrease after the maximum at about 3.5 K for **1** suggested long-range ordering occurring as a result of interchain AF interactions, while no decrease down to 2 K was observed for **2**, indicating weaker interchain interactions due to larger interchain distances.

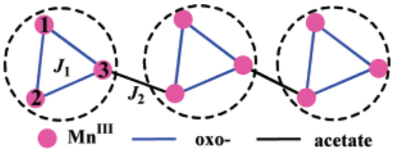
Undoubtedly, the coupling interaction (J_1) through oxo bridges within the Mn^{III}_3O cluster should be much stronger than that through acetate bridges (J_2); thus, the magnetic chains can be viewed as in Chart 1 on the basis of an approximate model,[9] where the near-equilateral trinuclear [Mn_3] was treated as the repeat unit of a uniform chain:

---

(7) Crystal data for **1**: $C_{32}H_{33}Mn_3N_6O_9$, $M = 810.46$, monoclinic, $P2_1/n$, $a = 20.309(4)$ Å, $b = 7.625(2)$ Å, $c = 21.554(4)$ Å, $\beta = 91.78(3)°$, $V = 3336.2(12)$ Å^3, $Z = 4$, $D_c = 1.614$ Mg m^{-3}, R1 = 0.0502, wR2 = 0.1559, $T = 173(2)$ K, $\mu = 1.182$ mm^{-1}, and $S = 1.119$. Crystal data for **2**: $C_{36}H_{43}Mn_3N_6O_{10}$, $M = 884.58$, monoclinic, $P2_1/n$, $a = 7.803(2)$ Å, $b = 24.457(5)$ Å, $c = 21.302(4)$ Å, $\beta = 99.23(3)°$, $V = 4012.4(14)$ Å^3, $Z = 4$, $D_c = 1.464$ Mg m^{-3}, R1 = 0.0495, wR2 = 0.1327, $T = 173(2)$ K, $\mu = 0.991$ mm^{-1}, and $S = 1.069$.

(8) (a) Liu, W.; Thorp, H. H. *Inorg. Chem.* **1993**, *32*, 4102. (b) BVS values for the Mn^{III} and O^{2-} ions are 2.93−3.18 and 1.86−1.87, respectively.

Chart 1



$\hat{H} = -2J_1\{\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3 + \hat{S}_3\hat{S}_1\}$ (for the trinuclear [Mn$_3$]);[10] $\hat{H} = -J_2\sum S_{T,i}S_{T,i+1}$ (S_T for [Mn$_3$] as a classical system). However, the fitting could not reach convergence. Thus, a further approximation was executed: both J_2 and interchain (J_3) interactions were treated as an intermolecular interaction ($J' = J_2 + J_3$) by mean-field theory[11] with the magnetic susceptibility expression

$$\chi_M = \frac{\chi_{trimer}}{1 - \frac{2J'}{Ng^2\mu_B{}^2}\chi_{trimer}} \qquad (1)$$

The experiment data above 40 K were least-squares fit to give the best sets of parameters $J_1 = -3.01$ cm^{-1}, $J' = 0.32$ cm^{-1}, $g = 1.88$, and $R = 1.9 \times 10^{-6}$ for **1** and $J_1 = -3.21$ cm^{-1}, $J' = 0.68$ cm^{-1}, $g = 1.93$, and $R = 4.5 \times 10^{-6}$ for **2** ($R = \sum[(\chi_M T)_{obs} - (\chi_M T)_{calcd}]^2/\sum[(\chi_M T)_{obs}]^2$). The results well confirmed the intracluster AF couplings in **1** and **2** through oxo bridges, which are much weaker than those in carboxylato-Mn$^{III}{}_3$O clusters.[5b,e] Because J_2 is the predominant intercluster interaction, the positive J' indicates that the couplings, though acetate bridges, are ferromagnetic. The larger J' for **2** might result from the weaker interchain AF interactions (J_3), which is in accord with the above observation. It is known that the equilateral [M$_3$O] triangle undergoes a magnetic Jahn−Teller effect,[12] and an isosceles model[13] was then tried to fit the magnetic susceptibilities of **1** and **2**, which, however, did not give reasonable results. It should be noted to observe ferromagnetic couplings through the anti−anti acetato bridges here, which was found to give AF couplings in [Mn(salen)(OAc)].[14] It would be expected to construct new single-chain magnets through further increases of the interchain distances.

Long-range ordering for **1** was confirmed by field-cooled magnetizations (FCMs) and ac susceptibilities at different frequencies of 1−100 Hz in zero dc field (Figure S4 in the Supporting Information). The FCM at 800 Oe for **1** (Figure 2b) and the real part of the ac susceptibility display maxima at about 3.2 K, while the out-of-phase component (χ_{ac}'') remains zero, clearly indicating the occurrence of three-dimensional AF ordering. The transition temperatures (T_N) were estimated as 3.2 K by the peak of χ_{ac}' vs T. The maxima in χ_M vs T plots gradually disappeared when the applied fields increased, suggesting a field-induced metamagnetic behavior. The ac susceptibilities for **2** further suggested that no long-range ordering occurred above 2 K.

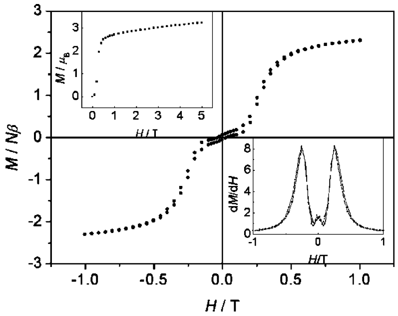


Figure 3. Field-dependent magnetization and hysteresis loop of **1**.

As shown in Figure 3, the field-dependent magnetization of **1** measured at 1.8 K showed a sigmoidal shape, confirming the metamagnetic behavior: the magnetization (M) first increases slowly with the increase of the field (H) due to interchain AF interactions and then shows a sharp transition at about 2000 G to a ferrimagnetic-like state with a saturated value of about 3.5 Nβ at 5 T, which is inconsistent with one Mn^{III} ion from the AF-coupled trinuclear [Mn$^{III}{}_3$]. The critical field (H_c) was determined as 2500 G by the peak position of dM/dH. Interestingly, isothermal magnetization measurement showed a hysteresis loop with a coercive field of 400 G, which may be due to the tune of magnetic anisotropy of Mn^{III} ions. For **2**, the field-dependent magnetization measured at 1.8 K (Figure S5 in the Supporting Information) showed an abrupt increase at the beginning of the field and became somewhat saturated to about 3.5 Nβ at 5 T.

In summary, we have synthesized two chain complexes (**1** and **2**) built with Mn$^{III}{}_3$O units for the first time. Magnetic studies indicated that the intracluster antiferromagnetically coupled Mn$^{III}{}_3$O units in both chains were ferromagnetically coupled though acetate bridges and the interchain AF interactions of **1** were stronger than those of **2**, resulting in a field-induced metamagnetic behavior in **1** and no magnetic order in **2** at above 2 K. The title compounds are expected to be good prototypes to afford Glauber chains[15] with slow magnetic relaxation. Further investigations in using different bridges, solvents, and/or substituted groups on ppz^{2-} to achieve new structural and magnetic properties are in progress.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (Grant 20301014), the Japan Society for the Promotion of Science, and the Innovation Foundation for Young Scientific Talents of Fujian Province of China (Grant 2002J004).

Supporting Information Available: Three-dimensional structures, plots of $\chi_M{}^{-1}$ vs T, ac susceptibilities, field-dependent magnetizations, and IR spectra of **1** and **2** and X-ray crystallographic data in CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

IC060159Y

---

(9) Zhang, Y. Z.; Wei, H. Y.; Pan, F.; Wang, Z. M.; Chen, Z. D.; Gao, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 5841.

(10) Kambe, K. *J. Phys. Soc. Jpn.* **1949**, *5*, 48.

(11) (a) Myers, B. E.; Berger, L.; Friedberg, S. *J. Appl. Phys.* **1969**, *40*, 1149. (b) O'Connor, C. J. *Prog. Inorg. Chem.* **1982**, *29*, 203.

(12) Murao, T. *Phys. Lett.* **1974**, *49A*, 33.

(13) Cannon, R. D.; Jayasooriya, U. A.; Wu, R.; arapKoske, S. K.; Stride, J. A.; Nielsen, O. F.; White, R. P.; Kearley, G. J.; Summerfield, D. *J. Am. Chem. Soc.* **1994**, *116*, 11869.

(14) (a) Davis, J. E.; Gatehouse, B. M.; Murray, K. S. *J. Chem. Soc., Dalton Trans.* **1973**, 2523. (b) Kennedy, B. J.; Murray, K. S. *Inorg. Chem.* **1985**, *24*, 1552.

(15) (a) Glauber, R. J. *J. Math. Phys.* **1963**, *4*, 294. (b) Miyasaka, H.; Clérac, R. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 1725.