A Novel Octanuclear Manganese Cluster with $[Mn^{II}_4(\mu_4\text{-O})]$ Core

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The reaction of $MnCl_2 \cdot 4H_2O$ with 2-aminoethanethiol (= Haet) under anaerobic conditions afforded yellow plate crystals of octanuclear manganese complex $[Mn_4(\mu_4\text{-O})\{Mn(aet)_3\}_4]Cl_2 \cdot MeOH \cdot 4H_2O$. A complex molecule consists of four *fac*(*S*)-$[Mn(aet)_3]$ units linked to $Mn^{II}_4(\mu_4\text{-O})$ core by thiolato bridges. Magnetic susceptibility measurements revealed the presence of antiferromagnetic interactions through μ_4-oxo and μ_2-thiolato bridges.

Cluster chemistry is of current interest from viewpoints of magnetic and bioinorganic chemistry.[1] To explore synthetic routes for preparing new transition-metal cluster, the choice of bridging ligands is important. Carboxylato- and oxo-bridges have been often used for preparing large molecules,[2] and strong Lewis base of thiolate was also known to form large molecules. It is pointed out that tris(thiolato)-type complexes *fac*(*S*)-$[M(aet)_3]$ (Haet = 2-aminoethanethiol) act as an effective tridentate-*S*,*S*,*S* complex-ligands toward transition metal ions (Scheme 1).[3] Trinuclear complexes $[M'\{M(aet)_3\}_2]^{3+}$ ($M = Rh^{III}$ and Ir^{III}; $M' = Co^{III}$),[3b,3c] pentanuclear complexes $[M'_3\{M(aet)_3\}_2]^{6+ \text{ or } 3+}$ ($M = Cr^{III}$, Co^{III}, Rh^{III}, and Ir^{III}; $M' = Hg^{II}$ and Ag^{I}),[3d–3h] and octanuclear complexes $[M'_4(\mu_4\text{-O})\{M(aet)_3\}_4]^{6+}$ ($M = Cr^{III}$, Co^{III}, Rh^{III}, and Ir^{III}; $M' = Zn^{II}$ and Co^{II})[3i–3m] were prepared by stepwise reactions of $[M'(aet)_3]$ unit with additional metal ions.

However, there are not many reports of paramagnetic octanuclear clusters.[4] We report here synthesis and structure of an octanuclear manganese cluster $[Mn^{II}_4(\mu_4\text{-O})\{Mn^{II}(aet)_3\}_4]Cl_2 \cdot MeOH \cdot 4H_2O$ (**1**$\cdot Cl_2 \cdot MeOH \cdot 4H_2O$).

Synthesis was performed under nitrogen atmosphere by using Schlenk techniques. A solution of $MnCl_2 \cdot 4H_2O$ (198 mg, 1.0 mmol) in methanol (10 cm^3) was added to the mixture of 2-aminoethanethiol hydrochloride (170 mg, 1.5 mmol) and triethylamine (202 mg, 2.0 mmol) in methanol (20 cm^3). The resulting solution was allowed to stand for one month at room temperature to give yellow plate crystals of **1**$\cdot Cl_2 \cdot MeOH \cdot 4H_2O$.[5]

$\mathbf{1}^{2+}$ is composed of four *fac*(*S*)-$[Mn^{II}(aet)_3]^-$ units and one $[Mn^{II}_4(\mu_4\text{-O})]^{6+}$ unit (Figure 1). In the octanuclear core, four Mn^{II} ions (Mn1–Mn4) are bound to a central oxide ion in a tetrahedral geometry to construct $[Mn^{II}_4(\mu_4\text{-O})]^{6+}$ core, which is linked to four *fac*(*S*)-$[Mn(aet)_3]$ units via thiolato bridges, giving tetrahedral symmetrical cage. Tetrahedral coordination sites of each Mn ion in the $Mn_4(\mu_4\text{-O})$ core are occupied by one μ_4-O atom and three μ_2-S atoms from aet. The average Mn–O and Mn–S distances are 2.049 and 2.451 Å, respectively, which lie on the typical coordination bond length for tetrahedral Mn^{2+} ions.[4a,6] The Mn–O–Mn angles range from 106.46(9) to 111.58(10)° with the average interatomic distance (Mn–Mn) of 3.34 Å. In the four $[Mn^{II}(aet)_3]^-$ units, all Mn(II) ions have distorted octahedral geometry with three N atoms and three S atoms from three bidentate aet ligands. The average Mn–N and Mn–S distances are 2.296 and 2.603 Å, respectively, and the Mn–S–Mn angles are in the range of 98.53(4) to 107.79(4)°. Charge considerations and coordination bond

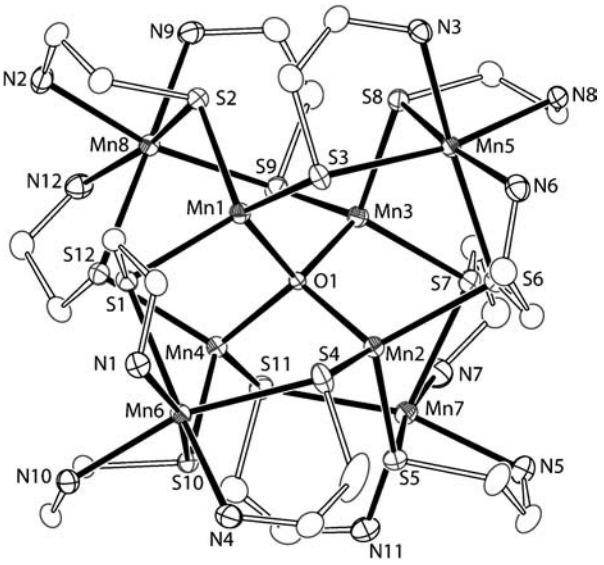
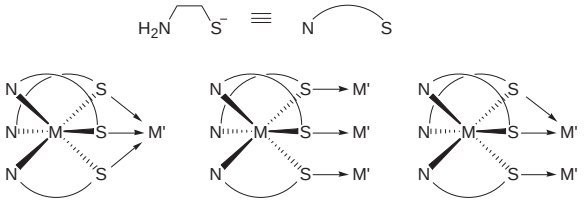


Figure 1. An ORTEP drawing of **1**. Selected bond lengths (Å): Mn1–O1 = 2.054(2), Mn(1)–S(2) = 2.4529(10), Mn(1)–S(1) = 2.4533(10), Mn(1)–S(3) = 2.4543(10), Mn(2)–O(1) = 2.043(2), Mn(2)–S(4) = 2.4260(12), Mn(2)–S(6) = 2.4391(10), Mn(2)–S(5) = 2.4471(11), Mn(3)–O(1) = 2.048(2), Mn(3)–S(8) = 2.4544(10), Mn(3)–S(7) = 2.4561(10), Mn(3)–S(9) = 2.4556(11), Mn(4)–O(1) = 2.049(2), Mn(4)–S(12) = 2.4492(10), Mn(4)–S(11) = 2.4604(11), Mn(4)–S(10) = 2.4690(10), Mn(5)–N(8) = 2.266(3), Mn(5)–N(6) = 2.292(3), Mn(5)–N(3) = 2.299(3), Mn(5)–S(3) = 2.5993(10), Mn(5)–S(6) = 2.6007(10), Mn(5)–S(8) = 2.6403(10), Mn(6)–N(1) = 2.286(3), Mn(6)–N(10) = 2.312(3), Mn(6)–N(4) = 2.316(3), Mn(6)–S(4) = 2.5725(11), Mn(6)–S(1) = 2.6197(10), Mn(6)–S(10) = 2.6278(10), Mn(7)–N(7) = 2.273(4), Mn(7)–N(5) = 2.285(3), Mn(7)–N(11) = 2.325(3), Mn(7)–S(11) = 2.5906(11), Mn(7)–S(5) = 2.5921(12), Mn(7)–S(7) = 2.6161(11), Mn(8)–N(12) = 2.278(3), Mn(8)–N(2) = 2.311(3), Mn(8)–N(9) = 2.314(3), Mn(8)–S(9) = 2.5891(10), Mn(8)–S(12) = 2.5890(10), Mn(8)–S(2) = 2.6010(11).



Scheme 1. Bridging mode of *fac*(*S*)-$[M(aet)_3]$.

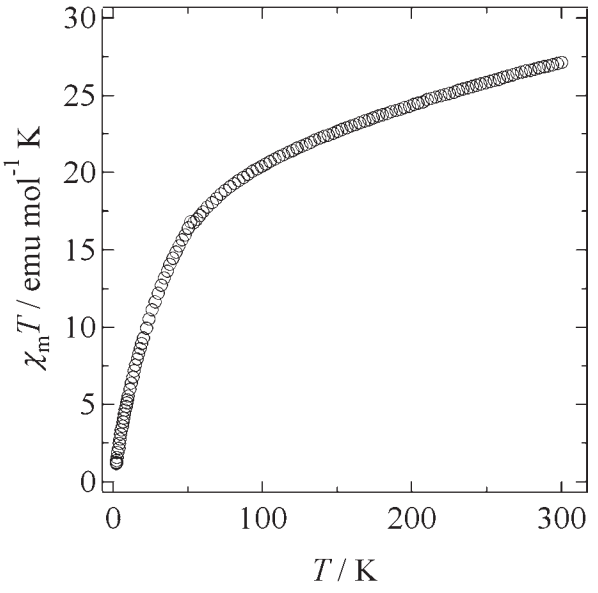


Figure 2. $\chi_m T$ vs. T plot for complex **1**·Cl_2·MeOH·$4H_2O$.

lengths confirm that all manganese ions are +2 ions. The compound crystallized in monoclinic space group $C2/c$. Each *fac*(*S*)-[$Mn(aet)_3$]$^-$ core has Δ or Λ configuration; however, they are related by mirror planes. It is not clear why **1** is racemic, although the bridging sulfur atoms are chiral centers. Absence of strong intermolecular interactions such as Coulomb interactions and hydrogen bonds might be responsible for racemate.

Magnetic susceptibility measurements for **1**·Cl_2·MeOH·$4H_2O$ were performed in the temperature range of 1.8–300 K (Figure 2).[7] The $\chi_m T$ value at 300 K is 27.12 emu mol^{-1} K, which is smaller than the value expected for uncorrelated eight Mn(II) ions (35 emu mol^{-1} K with $g = 2$). The $\chi_m T$ value gradually decreased as the temperature was lowered, and reached the value of 1.18 emu mol^{-1} K at 1.8 K. The Curie–Weiss plot gave a negative Weiss constant ($C = 33.87$ emu mol^{-1} K and $\theta = -76.64$ K), which suggested relatively strong antiferromagnetic interactions being operative among manganese ions. Thiolato-bridged Mn(II) complexes have been reported to show antiferromagnetic interaction ($J \approx -10$ cm^{-1}).[6] In **1**, bridging bond angles by the thiolates are nearly the same as the previously reported values; therefore, both thiolato- and oxo-bridges propagate the antiferromagnetic interactions. It is noted that the temperature dependence of $\chi_m T$ values approaching to zero is indicative of the absence of spin frustration.

In summary, an octanuclear manganese complex **1** with uncommon $Mn^{II}_4(\mu_4\text{-O})$ core was successfully synthesized under anaerobic conditions.

We acknowledge the financial supports by the COE and TARA projects in University of Tsukuba and by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References and Notes

1 a) G. Christou, D. Gatteschi, D. Hendrickson, R. Sessoli, *MRS Bull.* **2000**, *25*, 66. b) S. Mukhopadhyay, S. K. Mandal, S. Bhaduri, W. H. Armstrong, *Chem. Rev.* **2004**, *104*, 3981.

2 a) T. Lis, *Acta Crystallogr., Sect. B* **1980**, *36*, 2042. b) R. W. Saalfrank, I. Bernt, E. Uller, F. Hampel, *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2482. c) A. Caneschi, A. Conia, S. J. Lippard, *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 467. d) K. L. Taft, C. D. Delfs, G. C. Papaefthymiou, S. Foner, D. Gatteschi, S. J. Lippert, *J. Am. Chem. Soc.* **1994**, *116*, 823. e) A. Caneschi, A. Conia, A. C. Fabretti, D. Gatteschi, *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1295.

3 a) T. Konno, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 627. b) T. Konno, S. Aizawa, K. Okamoto, J. Hidaka, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 792. c) T. Konno, K. Nakamura, K. Okamoto, J. Hidaka, *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2582. d) K. Okamoto, T. Konno, Y. Kageyama, J. Hidaka, *Chem. Lett.* **1992**, 1105. e) K. Okamoto, Y. Kageyama, T. Konno, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2573. f) T. Konno, K. Okamoto, *Inorg. Chem.* **1997**, *36*, 1403. g) T. Konno, T. Tokuda, T. Suzuki, K. Okamoto, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1049. h) M. Hirotsu, Y. Nozaki, T. Yoshimura, W. Mori, T. Konno, *Mol. Cryst. Liq. Cryst.* **2002**, *379*, 461. i) T. Konno, K. Okamoto, J. Hidaka, *Chem. Lett.* **1990**, 1043. j) T. Konno, K. Okamoto, J. Hidaka, *Inorg. Chem.* **1991**, *30*, 2253. k) T. Konno, T. Nagashio, K. Okamoto, J. Hidaka, *Inorg. Chem.* **1994**, *33*, 538. l) T. Konno, K. Okamoto, J. Hidaka, *Bull. Chem. Soc. Jpn.* **1994**, *67*, 101. m) K. Okamoto, T. Konno, J. Hidaka, *J. Chem. Soc., Dalton Trans.* **1994**, 533.

4 a) F. A. Cotton, L. M. Daniels, L. R. Falvello, J. H. Matonic, C. A. Murillo, X. Wang, H. Zhou, *Inorg. Chim. Acta* **1997**, *266*, 91. b) F. A. Cotton, L. M. Daniels, G. T. Jordan, IV, C. A. Murillo, I. Pascual, *Inorg. Chim. Acta* **2000**, *297*, 6. c) B. Beagley, C. A. McAuliffe, P. P. MacRory, P. T. Ndifon, R. G. Pritchard, *J. Chem. Soc., Chem. Commun.* **1990**, 309. d) P. Beagley, A. G. Mackie, P. P. Matear, C. A. McAliffe, P. T. Ndifon, R. G. Pritchard, *J. Chem. Soc., Dalton Trans.* **1992**, 1301. e) C. S. Alvarez, A. D. Bond, D. Cave, M. E. G. Mosquera, E. A. Harron, R. A. Layfield, M. McPartlin, J. M. Rawson, P. T. Wood, D. S. Wright, *Chem. Commun.* **2002**, 2980.

5 Crystal data for **1**·MeOH·$4H_2O$: $C_{26}H_{72}N_{12}Cl_2Mn_8O_5S_{12}$, MW 1528.13, monoclinic, space group $C2/c$, $a = 28.8096(17)$, $b = 21.0232(12)$, $c = 24.2712(14)$ Å, $\beta = 117.1940(10)^\circ$, $V = 13075.4(13)$ Å^3, $Z = 8$, $D_{calcd} = 5.588$ Mg m^{-3}, $F(000) = 22372$, μ(Mo Kα) = 7.139 mm^{-1}, 38282 reflections measured, 12831 unique ($R_{int} = 0.0293$), $R1 = 0.0358$, $wR2 = 0.0525$ (all data).

6 M. Mikuriya, F. Adachi, H. Ishikawa, M. Handa, M. Koikawa, H. Ōkawa, *Bull. Chem. Soc. Jpn.* **1994**, *67*, 3263.

7 **1**·Cl_2·MeOH·$4H_2O$ extremely sensitive to the air. The sample for magnetic susceptibility measurement was sealed in a quartz tube under an anaerobic condition.

Published on the web (Advance View) March 25, 2006; DOI 10.1246/cl.2006.440