A Novel One-Dimensional Chain Complex Composed of Oxo-Centered Trinuclear Manganese Clusters

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A new linear chain complex of oxo-centered trinuclear manganese clusters, $[\{Mn^{III}{}_2Mn^{II}O(O_2CCHCl_2)_6(H_2O)\}\{Mn(O_2CCHCl_2)_2(H_2O)_4\}]_n$ (**1**), has been synthesized by treatment of a mixture of $Mn(OAc)_2\cdot 4H_2O$ and dichloroacetic acid in dichloromethane with $KMnO_4$. In this complex chains are formed by hydrogen bonding between carboxylate oxygens and coordinated water molecules, forming a two-dimensional structure. Antiferromagnetic coupling was observed by variable-temperature magnetic measurements.

Introduction

In the past few decades manganese chemistry has attracted much attention for the design of a new class of clusters for two reasons: first, to develop polynuclear manganese clusters as models for the water oxidation center of photosynthetic electron-transport chains in plants,[1] and second, to design new single-molecule magnets.[2] The first single-molecule magnetic behavior was observed in $[Mn_{12}O_{12}(OAc)_{16}(H_2O)_4]$ in 1993.[3] Single-molecule magnets (SMMs), as a prototype of nanomagnets, display an intramolecular magnetic hysteresis loop: each independent molecule in these materials possesses the ability to function as a magnetizable magnet owing to its intrinsic intramolecular properties rather than intermolecular interactions and long-range ordering.[4]

In the course of recent exploration of new manganese cluster complexes,[5] many oxo-centered trinuclear manganese carboxylate clusters with the common composition $[Mn_3O(O_2CR)_6L_3]$ have been synthesized and their physical properties studied extensively as model complexes for elucidating intramolecular electronic and magnetic interactions in clusters.[6−11] Furthermore, they have been used as a rich source of polynuclear complexes with a variety of interesting structural and physical properties.[12−14] Recently, we have focused our efforts on finding various synthetic routes to develop polynuclear manganese carboxylate clusters and were successful in synthesizing new Mn_6, Mn_8 and Mn_{18} clusters.[15,16] As part of our continuing interests to prepare new manganese clusters, we have studied the reaction of $Mn(OAc)_2\cdot 4H_2O$ with $KMnO_4$ in the presence of an excess amount of dichloroacetic acid in dichloromethane. Herein, we report the synthesis and magnetic properties of an unprecedented linear-chain complex of oxo-centered trinuclear Mn clusters $[\{Mn^{III}{}_2Mn^{II}O(O_2CCHCl_2)_6(H_2O)\}\{Mn(O_2CCHCl_2)_2(H_2O)_4\}]_n$ (**1**).

Results and Discussion

The reaction mixture of $Mn(O_2CMe)_2\cdot 4H_2O$ and dichloroacetic acid in dichloromethane solvent was treated with a fine powder of $KMnO_4$ with vigorous stirring to afford a dark brown solution. It is interesting to note that the same reaction in aqueous media gives $[Mn_{12}O_{12}(O_2CHCl_2)_{16}(H_2O)_4]$,[15] meaning that an aqueous medium provides a more acidic environment suitable for stabilizing higher oxidation state of manganese. Crystals suitable for X-ray crystallography were obtained by slow diffusion of *n*-pentane into a dichloromethane solution of **1**.

Complex **1** crystallizes in the monoclinic space group $P2_1/n$. The asymmetric unit of **1**, as depicted in Figure 1, consists of an oxo-centered trinuclear $[Mn_3(\mu_3\text{-}O)]^{6+}$ core and an $[Mn(H_2O)_4]^{2+}$ moiety. The manganese ions of the mixed-valent $[Mn^{II}Mn^{III}{}_2(\mu\text{-}O)]^{6+}$ core are bridged by six dichloroacetate ligands. The $[Mn(H_2O)_4]^{2+}$ moiety is bridged by Mn3 and the neighboring Mn1′ through dichloroacetates with a *syn-anti* conformation. One terminal water molecule is coordinated to Mn2 to give an octahedral geometry. On the basis of Jahn−Teller distortions and bond-valence sum calculations,[17,18] two manganese ions (Mn1 and Mn2) were assigned to Mn^{III}. The axial Mn1−O17 and Mn1−O13 bonds [1.830(5) and 1.951(5) Å, respectively] are shorter than the other equatorial bonds

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[2.034(5)−2.096(5) Å] due to Jahn−Teller contraction, while the axial Mn2−O4 and Mn2−O7 bonds [2.124(6) and 2.244(6) Å, respectively] are rather longer than the other equatorial bonds [1.818(5)−1.989(5) Å] due to a Jahn−Teller elongation effect. The Mn^{II} ions (Mn3 and Mn4) have uniform Mn−O bond lengths [Mn3−O: 2.119(6)−2.179(5) Å; Mn4−O: 2.149(7)−2.220(6) Å]. The μ_3-O atom is essentially coplanar with the Mn_3 plane, with an O17−Mn_3 plane separation of only 0.002 Å. The oxo-bridged $Mn^{III}\cdots Mn^{III}$ distance of 3.224(2) Å is shorter than the oxo-bridged $Mn^{II}\cdots Mn^{III}$ distances of 3.401(2) and 3.467(2) Å, which are similar to a known $[Mn^{II}Mn^{III}{}_2(\mu\text{-}O)]^{6+}$ core.[8] The carboxylate-only bridged $Mn^{II}\cdots Mn^{II}$ distances are 4.893(2) Å and 4.899(2) Å. The adjacent chains are significantly associated via hydrogen bonding between the coordinated water molecule and the carboxylate oxygen atoms, as illustrated in Figure 2. The O···O distances of these hydrogen bonds are within the range 2.631(9)−3.067(9) Å. The interchain Mn···Mn distances of adjacent chains are 5.116 Å for Mn2···Mn2# (−*x*, 1 − *y*, −*z*) and 5.117 Å for Mn4···Mn4# (1 − *x*, −*y*, −*z*), indicating significant magnetic interactions between the chains.

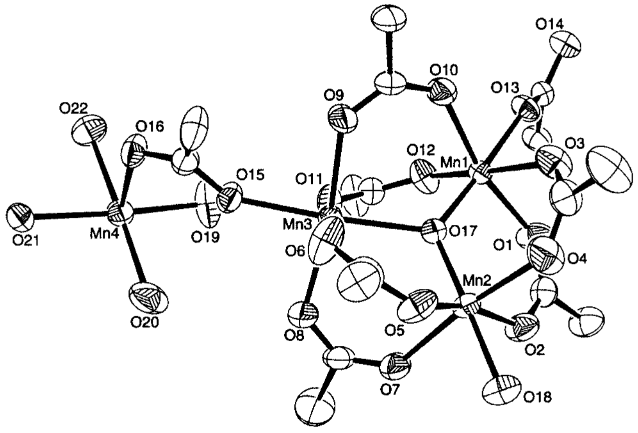

Figure 1. ORTEP diagram of **1** with atom numbering scheme; chlorine and hydrogen atoms are omitted for clarity; selected distances (Å): Mn1···Mn2 3.224(2), Mn1···Mn3 3.467(2), Mn2···Mn3 3.401(2), Mn3···Mn4 4.899(2), Mn1··· Mn4# (*x*, *y* − 1, *z*) 4.893(2)

Variable-temperature magnetic susceptibility data were measured for compound **1** from 2.0 to 300 K at 500 Oe. The resulting plot of $\chi_m T$ versus T for **1** is given in Figure 3. The $\chi_m T$ value is 14.9 $cm^3 \cdot K \cdot mol^{-1}$ at 300 K, which is in good agreement with the spin-only value expected for high-spin, non-interacting $Mn^{II}{}_2Mn^{III}{}_2$ ions.

The spin Hamiltonian for the isotropic magnetic exchange interaction in a trinuclear Mn_3O unit is given in Equation (1).

$$\hat{H} = -2[J_{12}(\hat{S}_1 \cdot \hat{S}_2) + J_{23}(\hat{S}_2 \cdot \hat{S}_3) + J_{31}(\hat{S}_3 \cdot \hat{S}_1)] \qquad (1)$$

In complex **1**, there are two exchange parameters, $J = J_{12} = J_{31}$ for Mn^{II}-Mn^{III} interactions and $J' = J_{23}$ for the Mn^{III}-Mn^{III} interactions. The molar susceptibility is given by Equation (2) for the ground-state total spin of 1/2.[10] In this expression, the Weiss constant, θ, is introduced to roughly simulate interactions of paramagnetic species. Equation (3) represents the theoretical model for an $[Mn(H_2O)_4]^{2+}$ site. The intrachain exchange interaction of Mn^{II}-Mn^{II} might be quite weak, considering that the coupling constant has been estimated as only -0.20 cm^{-1} in a linear chain Mn^{II} complex bridged by a carboxylate ligand with a *syn-anti* bonding mode.[19] Furthermore, hydrogen-bond-mediated magnetic interactions between manganese ions are also weak.[20] Thus, based on these facts, the expected $\chi_m T$ value of **1** can be modeled with Equation (4).

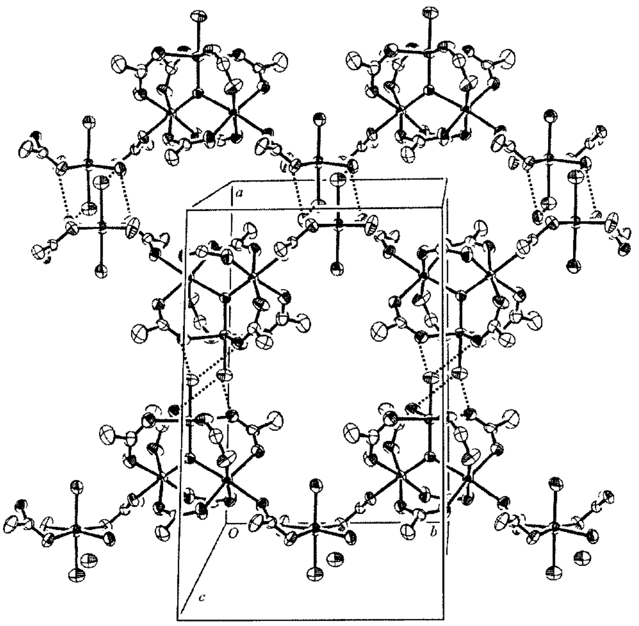

Figure 2. View down the *c*-axis showing the two-dimensional structure via interchain hydrogen bonding; chlorine atoms are omitted for clarity

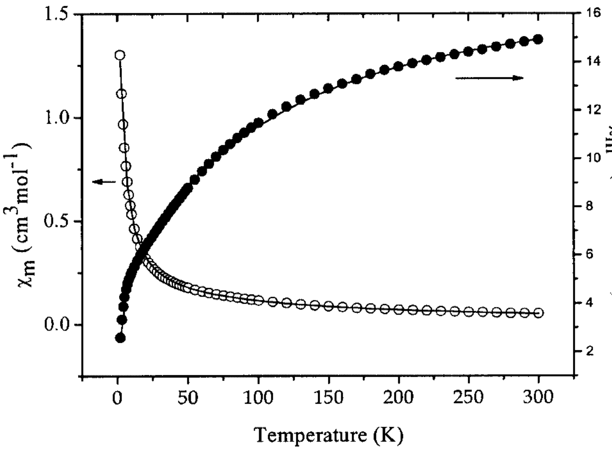

Figure 3. Temperature dependence of χ_{mol} (○) and $\chi_m T$ (·) at 500 Oe; the solid line represents the best fit of the data according to Equation (4)

$$\chi_{Mn_3O} = \frac{N\mu_B^2 g^2}{3k(T-\theta)} F(T;J,J') \qquad (2)$$

$$\chi_{Mn} = \frac{N\mu_B^2 g^2}{3k(T-\theta)} S(S+1) \qquad (3)$$

$$\chi_{\mathrm{m}} = \chi_{\mathrm{Mn_3O}} + \chi_{\mathrm{Mn}} \qquad (4)$$

The susceptibility data are fitted reasonably well by Equation (4), as shown in Figure 3. The fitting parameters are $J = -5.95$ cm^{-1}, $J' = -9.52$ cm^{-1}, $g = 2.16$, $\theta = -2.4$ K. The J, J', and g values are similar to the values for other mixed-valent $\mathrm{Mn^{II}Mn^{III}{}_2O}$ complexes.[8] The θ value of −2.4 K implies that paramagnetic centers such as the $[\mathrm{Mn(H_2O)_4}]^{2+}$ moiety and the $\mathrm{Mn_3O}$ units interact antiferromagnetically through intrachain bridging carboxylate bonds as well as interchain hydrogen bonds.

Experimental Section

General Remarks: All reagents and solvents were purchased from commercial sources and used as received. Elemental analysis was carried out by the Analytical Laboratory of the Korea Basic Science Institute, Seoul. Infrared spectra were recorded on a Perkin−Elmer 16 PC spectrophotometer. Variable-temperature magnetic susceptibility measurements were carried out on a crystalline sample of **1** in the 2−300 K temperature range using a Quantum Design MPMS*XL* susceptometer equipped with a 50 kG magnet at magnetic fields of 500 Oe. The correction for the diamagnetism of the complex was estimated from Pascal's constants, and the magnetic data were corrected for diamagnetic contributions of the sample holder.

Preparation of 1: $\mathrm{Mn(O_2CMe)_2{\cdot}4H_2O}$ (2.02 g, 8.16 mmol) and dichloroacetic acid (12 mL) were dissolved in 8 mL of dichloromethane and treated with a fine powder of $\mathrm{KMnO_4}$ (0.51 g, 3.2 mmol) with vigorous stirring to afford a dark brown solution. After filtration to remove insoluble impurities a large amount of pentane was added to give a dark brown solid. Dark brown single crystals for X-ray analysis were obtained by slow diffusion of pentane into a dichloromethane solution of **1** at room temperature. $\mathrm{C_{16}H_{18}Cl_{16}Mn_4O_{22}}$ (1349.3): calcd. C 14.24, H 1.34; found C 14.18, H 1.35. IR (KBr): $\tilde{\nu}$ = 1677(vs), 1663(vs), 1623(vs), 1599(vs), 1396(vs), 1227(m), 956(w), 926(s), 781(m), 714(s), 676(s), 550(w) cm^{-1}.

X-ray Crystallographic Study: A dark brown crystal (0.30 × 0.30 × 0.20 mm^3) was selected and mounted on a glass fiber. Intensity data were collected on an Enraf−Nonius CAD4 Diffractometer equipped with monochromated Mo-K_α radiation (λ = 0.71073 Å). Unit-cell parameters were determined from a least-squares fit of 25 accurately centered reflections. These dimensions and other parameters, including conditions of data collection, are summarized in Table 1. Data were collected at 293 K in the ω/2θ scan mode. The absorption correction was performed by a semi-empirical psi-scan. The structure was solved by direct methods using the SHELXS-97 and refined with SHELXL-97 by full-matrix least-squares methods on F^2.[21] All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were included in their calculated positions. The C−H bond lengths were fixed and the U values were assigned based approximately on the U value of the attached atom. CCDC-207185 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystallographic data for complex **1**

Empirical formula	$\mathrm{C_{16}H_{18}Cl_{16}Mn_4O_{22}}$
Molecular weight	1349.26
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	18.966(2)
b (Å)	11.552(1)
c (Å)	22.626(4)
β [°]	113.78(1)
V (Å^3)	4536(1)
Z	4
ρ_{calc} (mg m^{-3})	1.976
F(000)	2648
μ (mm^{-1})	2.102
Temperature (K)	293(2)
$2\theta_{\max}$ (°)	50
Transmission factor	0.7515−0.9999
Reflections collected	8214
Independent reflections	7998 [R_{int} = 0.0424]
Observed reflections [$I > 2\sigma(I)$]	6203
Data/restraints/parameters	7998/0/524
Goodness-of-fit on F^2	1.074
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0692, wR_2 = 0.1789
R indices for all data	R_1 = 0.0969, wR_2 = 0.2180

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