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$Mn_2(H_2O)[O_2C(CH_2)_nCO_2]_2$ ($n = 3-12$): Replication of an Inorganic Monolayer in Three-Dimensional (Dicarboxylato)manganese(II)

YooJin Kim, EunWon Lee, and Duk-Young Jung*

Department of Chemistry-BK21, SungKyunKwan University, Suwon 440-746, Korea

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A series of novel manganese α,*ω*-dicarboxylates, $Mn_2(H_2O)[O_2C(CH_2)_nCO_2]_2$ ($n = 3-12$), were synthesized as single crystals or polycrystallines by the hydrothermal reaction of $MnCl_2$ with the corresponding dicarboxylic acid in the presence of base. $Mn_2(H_2O)[O_2C(CH_2)_3CO_2]_2$ and $Mn_2(H_2O)[O_2C(CH_2)_5CO_2]_2$ ($n = 3$ and 5) crystallized in the orthorhombic space group *Pbcm* (No. 15), with $a = 7.6701(6)$ Å, $b = 9.1156(4)$ Å, $c = 17.975(1)$ Å, and $Z = 4$ and with $a = 7.6089(8)$ Å, $b = 9.167(2)$ Å, $c = 23.070(3)$ Å, and $Z = 4$, respectively. Using various α,*ω*-dicarboxylates with different numbers of carbons in alkyl chains, the interlayer spacings of the manganese(II) compounds have been varied from 8.99 to 20.42 Å. Their organic chains between two terminal carboxylates are close-packed and self-assembled between Mn−O layers. The relative conformations of two terminal carboxylate groups determine the spacing groups of crystal structures. All the prepared manganese dicarboxylate compounds involve the replication of the local crystal structure in the Mn−O monolayer to present an antiferromagnetic interaction.

Introduction

There has been considerable interest in the study of magnetically coupled metal complexes with extended structures on account of the artificial two-dimensional (2D) Heisenberg system[1] as well as their potential applications in the field of molecular-based magnets.[2] Extensive works have been carried out in the field of the artificial 2D magnetic system of thin magnetic layers through physical deposition methods.[3] On the contrary, to build a three-dimensional framework with 2D characteristics in chemical compounds through “crystal engineering”, certain features of the bridging ligands connecting paramagnetic metal centers can be utilized since they play a critical role in the molecular arrangement in a solid-state structure. The ligands with two end functional groups such as α,*ω*-diphosphonate,[4] carboxyphosphonate,[5] and dicarboxylate[6] could yield a variety of crystal structures of coordination complex depending on synthetic conditions and their end functional groups.

Recently, we have initiated the synthetic method of novel organic−inorganic hybrid materials, $Mn_2(H_2O)[O_2C(CH_2)_4CO_2]_2$ (adipate, $n = 4$ (even number) in $Mn_2(H_2O)[O_2C(CH_2)_nCO_2]_2$), prepared by the hydrothermal method, which has the topology of well-aligned, closed-packed alkyl chains by self-assembly, containing 2D inorganic metal−oxygen interlayers.[6a] The conformation and crystal structure of α,*ω*-dicarboxylic acid may depend on the value of *n*, the number of carbons in the chain, which encouraged us to prepare the series of similar manganese dicarboxylate compounds. Herein, we present the synthesis, structure, and magnetic properties of new compounds $Mn_2(H_2O)[O_2C(CH_2)_nCO_2]_2$ ($n = 3$, glutarate; 5, pimelate; 6, suberate; 7, azelate; 8, sebacate; 9, undecanedioate; 10, dodecanedioate; 11, tridecanedioate; 12, tetradecanedioate) (hereafter referred to as MnDC-*n*), which constitute examples of replication of magnetic coupling in the same local structure of a Mn−O monolayer. Unlike previously reported 2D systems, the prepared compounds have a three-dimensional self-assembled organic moiety and inorganic monolayers in the crystal structure.

Experimental Section

Manganese(II) chloride tetrahydrate (99.99%), glutaric ($n = 3$), adipic ($n = 4$), pimelic ($n = 5$), suberic ($n = 6$), azelic ($n = 7$), sebacic ($n = 8$), undecanedioic ($n = 9$), dodecanedioic (n

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* Corresponding author. E-mail: dyjung@chem.skku.ac.kr. Fax: 82-31-290-7075.

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= 10), tridecanedioic ($n = 11$), and tetradecanedioic acid ($n = 12$) (99%), diglyme (2-methoxyethyl ether), and potassium hydroxide (99.99%) were used as received from Aldrich.

For the synthesis of MnDC-3, a mixture of 1.19 g (6.0 mmol) of $MnCl_2 \cdot 4H_2O$, 0.79 g (6.0 mmol) of glutaric acid, 6.2 mL (9.3 mmol) of 1.5 M KOH solution, and 1.0 mL (0.70 mmol) of diglyme with $MnCl_2$:glutaric acid:KOH ratio of 1:1.0:1.6 (pH = 4.60) was heated with 9 mL of distilled water in a 23 mL capacity Teflon-lined reaction vessel at 180 °C for 1 day and then cooled to room temperature. Colorless (slightly pale-red) platelike crystals of MnDC-3 were obtained. The single crystals of MnDC-4 compound were synthesized according to the previous procedure.[6a] Syntheses of other MnDC-*n* compounds ($n = 5-12$) were prepared by a method similar to that for MnDC-3.

Anal. Calcd for $C_{10}H_{14}Mn_2O_{12}$ (MnDC-3): C, 30.92; H, 3.61. Found: C, 31.06; H, 3.67. Calcd for $C_{12}H_{18}Mn_2O_{12}$ (MnDC-4): C, 34.60; H, 4.32. Found: C, 34.33; H, 4.25. Calcd for $C_{14}H_{22}Mn_2O_{12}$ (MnDC-5): C, 37.82; H, 4.96. Found: C, 38.29; H, 5.13. Calcd for $C_{16}H_{26}Mn_2O_{12}$ (MnDC-6): C, 40.66; H, 5.51. Found: C, 40.58; H, 5.68. Calcd for $C_{18}H_{30}Mn_2O_{12}$ (MnDC-7): C, 43.17; H, 6.00. Found: C, 43.33; H, 6.24. Calcd for $C_{20}H_{34}Mn_2O_{12}$ (MnDC-8): C, 45.42; H, 6.44. Found: C, 44.52; H, 6.30. Calcd for $C_{22}H_{38}Mn_2O_{12}$ (MnDC-9): C, 47.45; H, 6.83. Found: C, 47.80; H, 7.16. Calcd for $C_{24}H_{42}Mn_2O_{12}$ (MnDC-10): C, 49.28; H, 7.19. Found: C, 48.12; H, 6.62. Calcd for $C_{26}H_{46}Mn_2O_{12}$ (MnDC-11): C, 50.94; H, 7.51. Found: C, 52.09; H, 7.97. Calcd for $C_{28}H_{50}Mn_2O_{12}$ (MnDC-12): C, 52,45; H, 7.81. Found: C, 50.00; H, 7.71.

Powder X-ray diffraction was performed on a MAC Science 18XMF diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å). Infrared (IR) spectra were obtained in 4000−400 cm^{-1} range using a Nicolet 1700 FT-IR spectrometer. The samples were ground with dry KBr and pressed into a transparent disk. Elemental analyses were performed by the Inter-University Center of Natural Science Research Facilities in Seoul National University. Thermogravimetric analyses (TG) were conducted on a TA instruments SDT 2960 simultaneous TG in a nitrogen atmosphere using a heating rate of 10 °C/min from room temperature to 1000 °C.

Magnetic susceptibility measurements were taken with a Quantum Design SQUID MPMS-5S magnetometer at 100 G from 4.2 to 300 K for ground single crystals and polycrystalline samples of MnDC-*n*. Measured susceptibility data were corrected for the contribution of the sample holder.

Crystal data for MnDC-*n* (n = 3 and 5) were collected on a Siemens P4 automated four-circle diffractometer equipped with graphite monochromated Mo Kα radiation ($\lambda = 0.710\,79$ Å). A crystal of each sample was glued to a glass fiber and mounted on the goniometer. Initial random search on the crystal resulted in 39 peaks ($10.0 < 2\theta < 25.0°$) that could be indexed with monoclinic unit cell similar to the final crystallographic results. Data collections were performed in ω mode on an octant ($1.99 < \theta < 25.0°$). Three check reflections were measured every 100 reflections throughout data collection and showed no significant variations in intensity. Intensity data were corrected for Lorentz and polarization effects. Decay corrections were also made. An absorption correction was applied on the basis of ϕ-scan data of six averaged reflections. The structure were solved by direct methods (SHELX-86) and standard difference Fourier techniques (SHELX-97).[7]

Results and Discussion

Syntheses. The MnDC-*n* compounds ($n = 3-6$) were obtained as single crystals, but the other compounds of MnDC-*n* ($n = 7-12$) were obtained as polycrystallines with nearly 100% yield. The reaction temperature and the initial pH value of solutions are very critical to prepare MnDC-*n*. When the starting solution was more basic, different phases with larger interlayer spacings were obtained, and these products are now under investigation.[8] Various alkali-metal hydroxides have been used for synthesis and yield the same compound at similar pH value. The insolubility of the prepared compounds in both polar and nonpolar solvents is indicative of layered polymeric characteristic structures. The use of diglyme is very helpful to prepare the pure phase of MnDC-*n* with *n* values higher than 5 due to low solubility of long-chain dicarboxylic acid.

The infrared spectrum of MnDC-*n* exhibits several bands from 1550 to 1580 cm^{-1} and from 1330 to 1400 cm^{-1}, characteristic regions for ν_a(OCO) and ν_s(OCO) bands, respectively. This observation suggests that all oxygen atoms of the carboxylato groups coordinate to Mn ions in bridging modes.[9]

Two distinct mass loss regions around 200 and 300 °C are seen in the TGA of all MnDC-*n* compounds. The first one at 150−250 °C is due to dehydration of coordinated H_2O which is a similar value for the $Mn^{II}(H_2O)[O_2C(CH_2)_4CO_2]$ sample prepared under ambient pressure.[10] The second weight loss is observed at higher temperature in the range 300 °C which corresponds to decomposition of dicarboxylate groups to produce graphite in inert atmosphere. The initial decomposition temperatures in N_2 decrease with increasing numbers of CH_2 groups in the dicarboxylates. X-ray powder diffraction spectra for the products after 1000 °C heat treatment in nitrogen could be assigned to Mn_2O_3 and a small amount of unidentified manganese oxide phases.

Structural Analyses. Compounds MnDC-3 and MnDC-5 crystallized in the orthorhombic crystal system. The pattern of systematic absences observed in the data was consistent with either the space group *Pbca*2$_1$ or *Pbcm*. The centric space group *Pbcm* was assumed and confirmed by the successful solution and refinement of the structure. In the structural analysis of MnDC-3 and MnDC-5, manganese and oxygen atoms were first located and the carbon atoms were found by difference Fourier maps. All hydrogen atoms attached to carbons positions were program generated and included in the refinements as a riding model. The hydrogen on thew water molecule was refined separately according to electron density difference. Absorption corrections were applied using the SHELX-86 program. Refinements for parameters were performed by full-matrix least-squares analysis, with anisotropic thermal parameters for all non-hydrogen atoms and with isotropic ones for all hydrogen atoms. The value of the discrepancy indicates R (R_w), for all of the data, were 0.0241 (0.0686) for MnDC-3 and 0.0541 (0.115) for MnDC-5. A summary of crystal data for MnDC-*n* ($n = 3-6$) is presented in Table 1. Fractional atomic coordinates of MnDC-*n* (n = 3 and 5) are given in Table 2, and selected bond distances and angles in Table 3, along with the data of MnDC-4 for comparison.[6a] MnDC-6 was obtained as single crystals; however, the refinement of atomic

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Table 1. Crystal Data and Structure Refinement for MnDC-*n* ($n = 3-6$)

	MnDC-3	MnDC-4	MnDC-5	MnDC-6
formula	$C_{10}H_{14}Mn_2O_9$	$C_{12}H_{18}Mn_2O_9$	$C_{14}H_{22}Mn_2O_9$	$C_{16}H_{26}Mn_2O_9$
fw	388.10	416.15	444.20	472.25
cryst system	orthorhombic	monoclinic	orthorhombic	monoclinic
space group	*Pbcm* (No. 57)	*C*2/*c* (No. 15)	*Pbcm* (No. 57)	*C*2/*c* (No. 15)
T (K)	296(2)	297(2)	296(2)	295(2)
a (Å)	7.6017(6)	21.671(2)	7.6089(8)	26.54(2)
b (Å)	9.1156(4)	7.6023(7)	9.167(2)	7.617(7)
c (Å)	17.9749(12)	9.1452(9)	23.070(3)	9.188(8)
α (deg)	90	90	90	90
β (deg)	90	108.849(7)	90	105.27(6)
γ (deg)	90	90	90	90
V (Å^3)	1245.55(14)	1425.9(2)	1609.1(4)	1792(3)
Z	4	4	4	4
D_{calcd} (mg cm^{-3})	2.070	1.938	1.834	
abs coeff (mm^{-1})	2.073	1.818	1.618	
reflcns collcd	1134	1289	1404	
goodness-of-fit on F^2	1.097	1.085	1.140	
final R_1[a]	0.0241	0.0380	0.0541	
final wR_2[b]	0.0686	0.1012	0.1150	

[a] $R_1 = \Sigma| |F_o| - |F_c| |/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2]/\Sigma w(|F_o|^2)^2]^{1/2}$.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for MnDC-3 and MnDC-5

atom	x	y	z	U_{eq}[a]
		MnDC-3		
Mn(1)	7050(1)	567(1)	5245(1)	4(1)
O(1w)	9052(3)	2500	5000	19(1)
O(2)	8019(2)	−278(2)	4193(1)	24(1)
O(3)	6146(2)	2025(1)	6088(1)	20(1)
O(4)	9201(2)	−477(1)	5839(1)	19(1)
O(5)	4807(2)	1158(1)	4509(1)	16(1)
C(1)	5181(2)	3131(2)	6083(1)	14(1)
C(2)	4477(3)	3725(2)	6805(1)	20(1)
C(3)	4983(4)	2888(3)	7500	20(1)
C(4)	9525(4)	−238(3)	2500	22(1)
C(5)	9806(3)	−1149(2)	3202(1)	21(1)
C(6)	9508(3)	−266(2)	3907(1)	15(1)
		MnDC-5		
Mn(1)	7042(1)	570(1)	5194(1)	13(1)
O(1w)	9069(9)	2500	5000	22(2)
O(2)	8010(6)	−274(5)	4377(2)	23(1)
O(3)	6157(6)	2032(5)	5848(2)	20(1)
O(4)	9188(6)	−477(5)	5653(2)	18(1)
O(5)	4815(6)	1155(5)	4618(2)	18(1)
C(1)	5173(9)	3119(7)	5842(3)	15(1)
C(2)	4524(9)	3742(7)	6406(3)	18(2)
C(3)	4924(10)	2867(7)	6947(2)	19(1)
C(4)	4514(14)	3701(11)	7500	21(2)
C(5)	9815(15)	−1085(11)	2500	22(2)
C(6)	9527(10)	−218(7)	3058(3)	22(2)
C(7)	9784(9)	−1132(8)	3598(3)	21(2)
C(8)	9503(8)	−256(7)	4147(2)	13(2)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

positions was unsuccessful, which is ascribed to local disorder resulting from long alkyl chains between two terminal carboxylate groups. The unit cell parameters and the suggested space group (*C*2/*c*) could be obtained by use of single-crystal analyses for MnDC-6.

Figure 1 shows that the crystal structures of three MnDC-*n* compounds ($n = 3-5$) involve a three-dimensional extended framework with Mn−O monolayer. Self-assembled amphiphilic dicarboxylate ions drive close packing of alkyl chains with hydrophobic characteristics along a unique direction,[11] the *c*-axis in MnDC-*n* ($n = 3$ and 5, odd numbers) and *a*-axis in MnDC-*n* ($n = 4$, even number), respectively. In addition, hydrophilic carboxylate groups and water coordinate with manganese(II) cations. MnDC-3 and MnDC-5 adopt the *Pbcm* space group while MnDC-4 and MnDC-6 crystalline in the *C*2/*c* space group. It should be noted that the even and odd number compounds belong to the different crystal system due to different point symmetries of corresponding dicarboxylate ligands. As presented in Figure 1, in MnDC-3 and MnDC-5, dicarboxylate ligands are bound to manganese ions located along the direction of alkyl chains. On the contrary, the manganese ions are coordinated between dicarboxylate ligands which could be interpreted as displacement along the [011] direction in MnDC-4 compared with MnDC-3 or MnDC-5.

Figure 2 shows the $Mn(H_2O)_{1/2}[O_2C(CH_2)_nCO_2]$ ($n = 3-5$) unit which provides the fundamental structural motifs in the architecture of the three-dimensional Mn−O framework of MnDC-*n*. The alkyl chains with both even and odd carbon numbers have the trans conformation in MnDC-*n* and are surrounded by six nearest alkyl chains with regular distance of about 4.1Å, a value quite close to the chain−chain spacings observed in dense solid phases of alkyl chains, such as Langmuir monolayers of saturated alkyl chains.[12] We also note that the interlayer alkyl chains in the pillared layered structures are less dense compared to MnDC-*n* in this study.

MnDC-3 and MnDC-5 have similar conformations of two terminal carboxylate groups. MnDC-3 and MnDC-5 (n = odd) contain dicarboxylate ligands which have a mirror plane in the middle of the ligands, the crystallographic positions of carbons of the alkyl chains. C5 and C6 in MnDC-3 and C6−C8 in MnDC-5 are represented by symmetric operations. On the contrary, carbon atoms of the dicarboxylate ligand in MnDC-4 have all different coordinates and the planes of two terminal carboxylate groups ($O-C-O^-$) are perpendicular to each other. The different directions of two terminal carboxylate groups in even and odd numbers of alkyl chain carbons determine their crystal systems. It is known that α,ω-dicarboxylic acids ($HOOC(CH_2)_n$-

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for MnDC-*n* ($n = 3-5$)[a]

bond length and bond angle	MnDC-3	MnDC-5	bond length and bond angle	MnDC-4
Mn(1)−O(3)	2.129(1)	2.128(4)	Mn(1)−O(4)	2.130(2)
Mn(1)−O(5)^{a}	2.159(1)	2.165(5)	Mn(1)−O(5)^{a}	2.158(2)
Mn(1)−O(2)	2.172(2)	2.166(5)	Mn(1)−O(1)	2.165(2)
Mn(1)−O(4)	2.172(1)	2.171(4)	Mn(1)−O(3)	2.170(2)
Mn(1)−O(5)	2.224(1)	2.218(5)	Mn(1)−O(5)	2.232(2)
Mn(1)−O(1w)	2.370(1)	2.389(5)	Mn(1)−O(2w)	2.370(2)
O(3)−Mn(1)−O(1w)	82.86(4)	82.5(2)	O(4)−Mn(1)−O(2w)^{a}	83.16(5)
O(5)^{a}−Mn(1)−O(1w)	178.51(4)	179.0(1)	O(5)^{a}−Mn(1)−O(2w)	178.54(5)
O(2)−Mn(1)−O(1w)	83.32(4)	83.2(1)	O(1)−Mn(1)−O(2w)	83.36(5)
O(4)−Mn(1)−O(1w)	86.19(5)	86.2(2)	O(3)−Mn(1)−O(2w)	86.15(6)
O(5)−Mn(1)−O(1w)	101.63(5)	101.7(2)	O(5)−Mn(1)−O(2w)	101.33(6)
O(3)−Mn(1)−O(5)^{a}	95.66(5)	96.4(2)	O(4)−Mn(1)−O(5)^{a}	95.38(6)
O(3)−Mn(1)−O(2)	161.97(6)	161.7(2)	O(4)−Mn(1)−O(1)	162.37(7)
O(5)^{a}−Mn(1)−O(2)	98.11(5)	97.8(2)	O(5)^{a}−Mn(1)−O(1)	98.08(7)
O(3)−Mn(1)−O(4)	99.61(5)	99.8(2)	O(4)−Mn(1)−O(3)	100.40(6)
O(5)^{a}−Mn(1)−O(4)	94.16(5)	94.0(2)	O(5)^{a}−Mn(1)−O(3)	94.09(6)
O(2)−Mn(1)−O(4)	90.96(5)	90.6(2)	O(1)−Mn(1)−O(3)	89.96(7)
O(3)−Mn(1)−O(5)	91.42(5)	91.7(2)	O(4)−Mn(1)−O(5)	92.13(6)
O(5)^{a}−Mn(1)−O(5)	78.28(5)	78.4(2)	O(5)−Mn(1)−O(5)^{a}	78.73(6)
O(2)−Mn(1)−O(5)	80.10(5)	80.0(2)	O(1)−Mn(1)−O(5)	79.46(6)
O(4)−Mn(1)−O(5)	167.25(5)	166.9(2)	O(3)−Mn(1)−O(5)	166.14(7)

[a] Symmetry transformations used to generate equivalent atoms for MnDC-3 and MnDC-5: (a) $-x + 1, -y, -z + 1$; (b) $x, -y + 1/2, -z + 1$; (c) $-x + 2, -y, -z + 1$; (d) $x, y, -z + 3/2$; (e) $x, y, -z + 1/2$. Symmetry transformations used to generate equivalent atoms for MnDC-4: (a) $-x + 1, -y + 1, -z + 2$; (b) $-x + 1, y, -z + 3/2$; (c) $-x + 1, -y, -z + 2$; (d) $x - 1/2, y - 1/2, z$; (e) $x + 1/2, y + 1/2, z$.

COOH) have two different conformations, α- and β-forms, in the crystal structures where *n* is odd. There is a significant controversy to MnDC-*n* compounds since even member MnDC-*n* presents a conformation similar to that for the α-form diacids in the solid-state structure. The principal possibility taking place for such twisting in terminal carboxylate groups of MnDC-*n* ($n =$ even) is ascribed to electrostatic interaction between Mn(II) and carboxylates, compared to hydrogen bonding in simple α,ω-dicarboxylic acids.[11] Another interesting difference from diacid cases is that the packing of alkyl chains in both even and odd members of MnDC-*n* is a hexagonal type similar to that for even members of α,ω-dicarboxylic acids. The alternation of melting point and the vibration frequency were observed in MnDC-*n* compounds.[8]

MnDC-3 and MnDC-5 (odd members) belong to a symmetry different from that of MnDC-*n* even members. However, as shown in Figure 3, manganese atoms of MnDC-*n* ($n = 3-5$) occupy the crystallographic sites with an octahedral coordination of oxygens arising from five carboxylate ions (three syn−syn and two monatomic bonding modes) and one water molecule. Each MnO_6 octahedron is strongly distorted, and the Mn−O(water) bond length is the largest. The coordination Mn−O(water) bond length distances are 2.370(1) and 2.389(5) for MnDC-3 and MnDC-5 and 2.370(2) Å for MnDC-4, respectively. The coordinated water is consistent with the calculation of bond valence sums,[13] TGA behavior, and the broad O−H stretching band in IR spectra. The space groups of MnDC-3 and MnDC-4 are different; however, both compounds have the same arrangement of Mn−O constructing a thin hydrophilic layer between thick hydrophobic crystalline alkyl-chain overlays. This crystallographic similarity can be obtained by rotation of the carboxyl group in the MnDC-3 case. The edge- and corner-sharing MnO_6 polyhedra produce parallel zigzag chains, cross-linked by syn−syn mode carboxylate groups which have Mn···Mn separations of 3.632, 3.638, and 3.649 Å for MnDC-3, -4, and -5, respectively. The Mn···Mn separations are larger than 3.3 Å, where the possibility of metal−metal bonding could be excluded. Note that the coordination environments of the MnO_6 layer in MnDC-*n* compounds present less compact Mn−O−Mn connectivity compared with the terephthalate-based cobalt hydroxide, which has μ_3-O(hydroxyl)- and μ_2-O(carboxylato)-bridged $Co^{II}O_6$ layer similar to its parent hydroxide $Co(OH)_2$ containing a trigonal Co(II) arrangement.[6h]

X-ray Powder Diffraction. The peak intensities of experimental X-ray powder diffraction (XRPD) spectra were in good agreement with calculated ones simulated by single-crystal data (MnDC-3 and MnDC-4). The XRPD data of MnDC-*n* with $n = 7-12$ are shown in Figure 4, where the interlayer distance was found to depend essentially on the number of carbon atoms of the alkyl chain. The XRPD spectra for MnDC-*n* also show strongly enhanced peaks [(00*l*) for odd and (*h*00) for even number of *n*], which correspond to the interlayer spacing of the 2D inorganic layers, presumably expected because of alternative stacking of amphiphilic layers in the crystal structure. Figure 5 presents the plots of the variation in the interlayer distance with increasing numbers of carbon atoms in the alkyl chains of MnDC-*n* compounds. Using various α,ω-dicarboxylates with different numbers of carbons in the alkyl chains (from $n = 3$ to 12), the interlayer spacing of MnDC-*n* has been varied from 8.99 to 20.42 Å. The interlayer distance increases linearly with *n*, which means that alkyl chains exhibit the same conformation and are inclined at the same angle with respect to the Mn−O plane. The experimental data presented in Figure 5 fit the straight line $d = 1.269(1)n + 5.18(1)$, where *d* is the interlayer distance in Å. Assuming an extended conformation for the alkyl chain, this equation can be rewritten as $d = 1.27n \sin \alpha + \Delta$,[14] where α is

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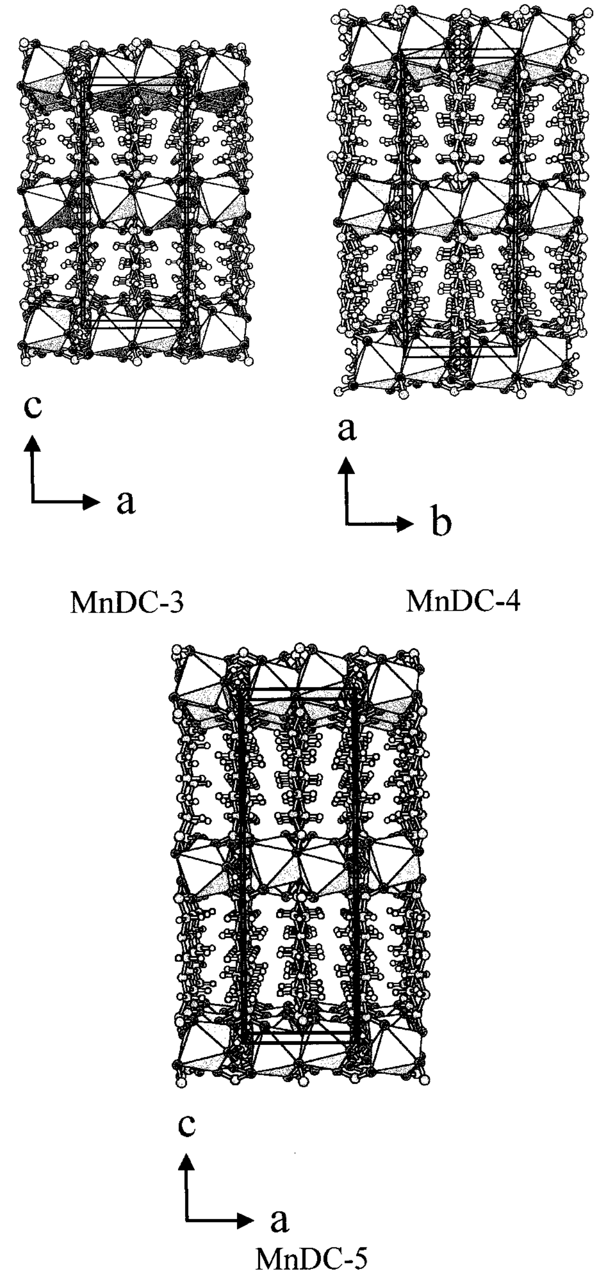

Figure 1. Views of the framework along the *b* direction of MnDC-3 and MnDC-5 and along *c* of MnDC-4. Polyhedra represent the MnO_6 octahedra, and black spheres corresponds to carbon atoms. The oxygen of water molecules locates between two edge-sharing MnO_6 polyhedra.

the angle between the alkyl chain axis and the Mn−O plane and Δ is the thickness of inorganic layer; for this case, $\alpha \approx 90°$, vertical to the Mn−O plane, and $\Delta = 5.18(1)$ Å, the thickness of MnO_6 layer involving carboxylic groups. These data support the structural similarity of all MnDC-*n* compounds though the MnDC-*n* of even *n* belongs to a space group different from that of odd *n*.

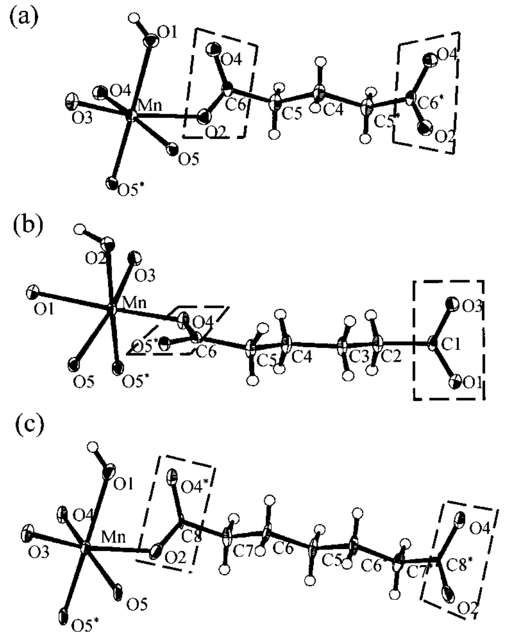

Figure 2. View of the $Mn(H_2O)_{1/2}[O_2C(CH_2)_nCO_2]$ unit of (a) MnDC-3, (b) MnDC-4, and (c) MnDC-5. Thermal ellipsoids are shown at 50% probability.

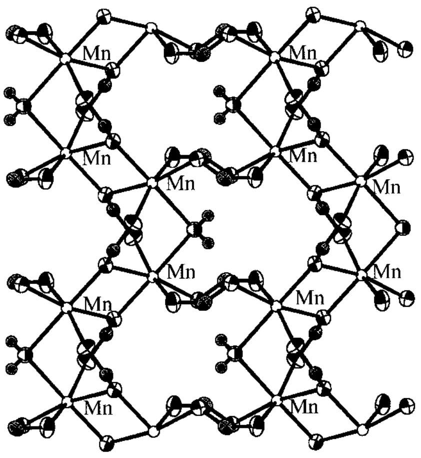

Figure 3. Two-dimensional network of the Mn−O layer in MnDC-3 (also the same in MnDC-4 and MnDC-5). The manganese and oxygen atoms are drawn with 50% probability ellipsoids. Carbons and hydrogens are drawn as empty balls.

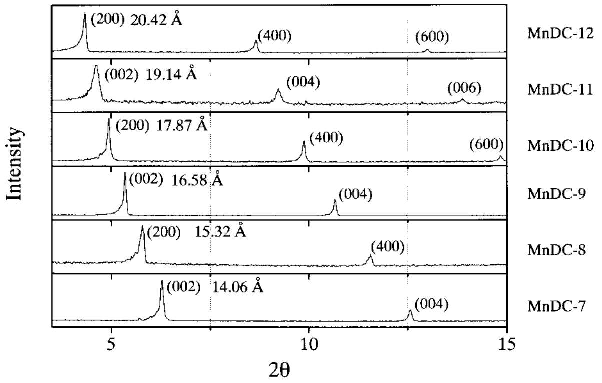

Figure 4. XRPD spectra for the polycrystalline samples of MnDC-*n* ($n = 7-12$).

Magnetic Measurements. Magnetic susceptibility data were recorded for all MnDC-*n* complexes from 5 K to room temperature. As one can see, the corresponding curves for MnDC-*n* are practically identical to each other (Figure 6). The values of χ_M were $\approx$0.01 $cm^3\ mol^{-1}$ at room temperature and increased with temperature, reaching a maximum of $\chi_M \approx 0.10$ $cm^3\ mol^{-1}$ at 10−15 K, and then decreased, tending to zero at 0 K. The $\chi_M T$ product decreased monotonically from $\approx$ 4.1 $cm^3\ mol^{-1}$ at ca. 300 K, which was close to the typical value for an $S = 5/2$ ion, assuming $g = 2.0$ (4.37 $cm^3\ mol^{-1}$ K). The $\chi_M T$ values decreased slowly with temperature to 3.0

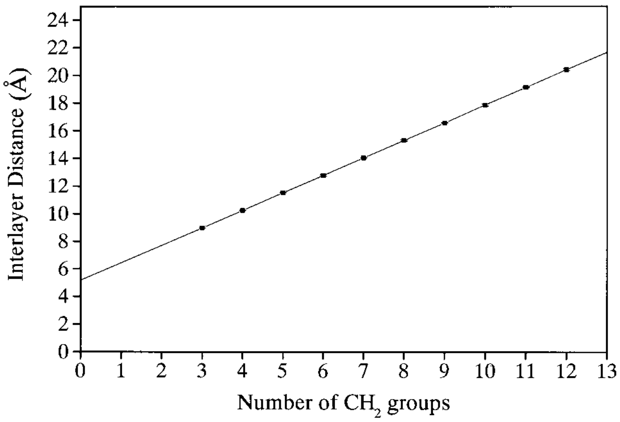

Figure 5. Interlayer distance as a function of the number of carbon atoms in the alkyl chain (n) for MnDC-n (n = 3−12).

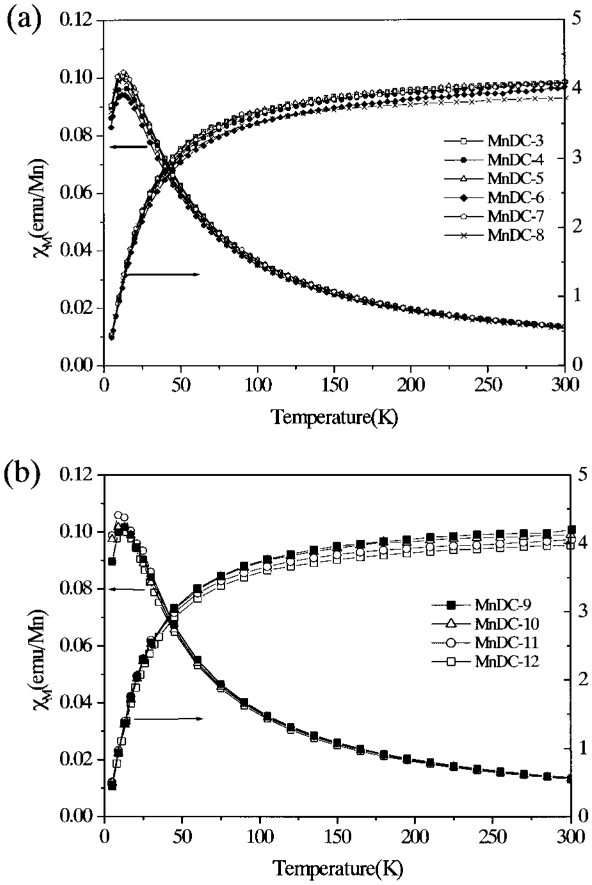

Figure 6. Temperature dependence of χ_M and $\chi_M T$ vs T for (a) MnDC-n (n = 3−8) and (b) MnDC-n (n = 9−12). The solid lines are the best fit to the experimental data using the Wagner−Friedberg model.

cm^3 mol^{-1} K at 50 K, followed by a further larger decrease, reaching a value of 0.5 cm^3 mol^{-1} K at 5 K for all the MnDC-n complexes. This behavior is typical for weak antiferromagnetic coupling between Mn(II) centers. At around 12 K, broad maximums in susceptibility curves indicate a low-dimensional antiferromagnet due to the 2D Mn−O−Mn array and the exchange paths mainly through Mn−O(water)−Mn and Mn−O(monatomic)−Mn as shown in Figure 3. For all MnDC-n compounds it appears that the temperatures of susceptibility maximum, $T_{\chi_{max}}$, remain constant at 13(1)K within experimental error limit as the interlayer spacing increases, which indicates that the length of alkyl chain does influence little on the intralayer nearest-neighbor magnetic exchange. The MnDC-n compounds have a single layer of MnO_6 polyhedra which involves the same *intra*layer crystal structure, at least for MnDC-n (n = 3−5) of which the crystal structures are fully solved, resulting in the similar short-range antiferromagnetic interactions.

The average effective magnetic moment for MnDC-n at room temperature is 5.73(6) μ_B/mol of Mn, which is generally observed in high-spin $Mn^{II}(3d^5)$ centers (5.65−6.10 μ_B)[15] and is close to 5.77 μ_B, the value reported for $Mn(O_2C(CH_2)_4CO_2)\cdot H_2O$ polycrystalline.[6f] Above ~50 K the data show good agreement with the Curie−Weiss law. The values of the Curie and Weiss constants determined are presented in Table 4, along with the effective moments, μ_{eff}, calculated from the Curie constants as well as the room temperature magnetic susceptibility values, similar to the spin-only moment of 5.92 μ_B for $S = 5/2$.

The magnetic susceptibility data for MnDC-n complexes may be analyzed according to two Heisenberg models for linear chains: (a) the scaling model of Wagner−Friedberg[16] with $S = 5/2$; (b) the Weng model[17] with coefficients generated by Hiller et al.[18] for $S = 5/2$, where $A = 2.9167$, $B = 208.04$, $C = 15.543$, $D = 2707.2$, and $x = |J|/2kT$. The isotropic Heisenberg Hamiltonian in both models is $\mathbf{H} = -J\Sigma \mathbf{S}_i\mathbf{S}_j$. Both the Wagner−Friedberg (solid lines in Figure 6) and Weng models with nearest-neighbor exchange gave good agreement for the susceptibility data between 5 and 300 K. Their calculated parameters are summarized in Table 4, including other magnetic parameters. Similar J and g values were obtained in all MnDC-n (n = 3−12) compounds, indicating that the basal spacings are rather insensitive to antiferromagnetic interaction between Mn(II) spin centers. The predominant magnetic coupling in MnDC-n is described in a first approach by one-dimensional Mn(II)−O−Mn(II) chains rather than 2D magnets. The values of J (average value of −2.1 cm^{-1}) are in accordance with the presence of μ_2-bridging oxygens resulting from carboxylato and water hydrate. It is generally assumed[19] that the μ_1-oxygens from bridging carboxylates between two Mn(II) ions are ineffective in transmitting the magnetic interaction to exhibit small negative values of J, as reported in other carboxylate compounds between −0.2 and −5 cm^{-1}.[20] In addition, experimental magnetic data were analyzed using the two-dimensional antiferromagnet model given by Rushbrooke and Wood.[21] However, the best fit using a 2D lattice could be carried out only for the data between 15 and 300 K, and the average values are $J = -0.7$ cm^{-1} and $g = 2.0$ for MnDC-n (n = 3−12) compounds.

Figure 7 shows field-cooled and zero-field-cooled magnetization data over the temperature range of 2−16

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Table 4. Magnetic Parameters of the MnDC-*n* Compounds (*n* = 3−12)

						Wagner[e]		Hiller[f]	
compd	C/cgs[a]	θ/K[b]	$\mu_{\mathrm{eff}}(C)$[c]	$\mu_{\mathrm{eff}}(\mathrm{RT})$[d]	T_{N}	J (cm^{-1})	g	J (cm^{-1})	g
MnDC-3	4.35	−17.92	5.92	5.75	5.1	−2.10	2.01	−1.98	2.01
MnDC-4	4.36	−20.52	5.93	5.75	4.7	−2.16	2.00	−2.04	2.00
MnDC-5	4.34	−17.81	5.91	5.75		−2.08	2.01	−1.96	2.01
MnDC-6	4.30	−22.61	5.89	5.70		−2.15	1.96	−2.00	1.96
MnDC-7	4.29	−18.36	5.88	5.75		−2.06	1.99	−1.91	1.98
MnDC-8	4.24	−16.21	5.85	5.69		−2.03	1.95	−1.89	1.94
MnDC-9	4.41	−19.18	5.97	5.80		−2.11	2.02	−1.96	2.00
MnDC-10	4.28	−17.67	5.87	5.70		−1.97	1.97	−1.83	1.96
MnDC-11	4.33	−18.04	5.91	5.72		−1.95	1.99	−1.81	1.98
MnDC-12	4.22	−18.44	5.84	5.60		−2.03	1.97	−1.87	1.95

[a] Curie constant (50−300 K). [b] Weiss constant (50−300 K). [c] $\mu_{\mathrm{eff}}(C) = 2.84(C)^{1/2}$; μ_{eff}(spin only) = 5.92 μ_{B}. [d] $\mu_{\mathrm{eff}}(\mathrm{RT}) = 2.84(\chi T)^{1/2}$, where $T \approx 300$ K. [e] Reference 16 (5−300 K). [f] Reference 18 (5−300 K).

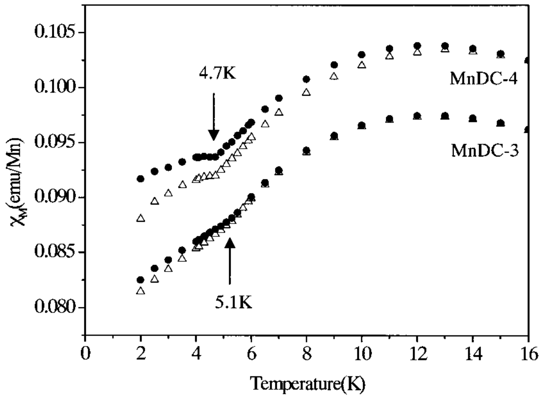

Figure 7. Magnetic susceptibility (χ_{M}) versus temperature measured at 1 kG for MnDC-3 and MnDC-4 and comparison of the data taken upon warming after cooling in zero-applied field (ZFC) and cooling in an applied field (FC), vertically offset by 0.005 emu/mol for clarity.

K for MnDC-3 and MnDC-4. The ordering temperature, T_{N}, is defined as the temperature of the onset of the sharp change of the magnetic susceptibility. The values of T_{N} are 5.1 K for MnDC-3 and 4.7 K for MnDC-4, respectively, which indicates the ordering transition to the "weak ferromagnetic" state.[22] Although the ferromagnetic moments for both compounds are not saturated down to 2 K, the ferromagnetic moments for MnDC-4 (*C*2/*c*) with lower symmetry in the crystal structure is greater than that for MnDC-3 (*Pbcm*).

The MnDC-*n* compounds show a similar 1D or 2D weak intralayer antiferromagnetic interaction between the Mn(II)−Mn(II) exchange resulting in the approximately same $T_{\chi_{\max}}$, and also the presence of a sudden increase in magnetic susceptibility in low temperature suggests that the total alignment of the spins is not produced to result in weak ferromagnetism through canted antiferromagnetism. It should be noted that the present MnDC-*n* compounds provide a new 2D layered magnetic materials where magnetic interactions are weaker than the manganese(II) phosphonates with T_{N} at around 12−15 K and $\mathrm{T}_{\chi_{\max}}$ at ~25 K, in the sample of polycrystalline[23] or Langmuir−Blodgett thin films.[24] The values of J for the 2D antiferromagnetic MnDC-*n* are determined as 1.0 cm^{-1} from the value of $\mathrm{T}_{\chi_{\max}}$ (=13 K) according to $|J| = 2kT_{\chi_{\max}}/[2.06S(S+1)]$.[25] It has been suggested that the variation in canting with increasing chain length is due to a very subtle change in structure of different Mn−alkylphosphonates[23,24] and the values of the weak ferromagnetic moments determined from the magnetization measurements are expected to present a lower limit to the actual values.[24] For MnDC-*n*, the transition temperatures, T_{N}, and the canting angles between magnetic moments are also expected to be varied through changes in the alkyl chain length (the value of *n*) as in the case of manganese phosphonate compounds. Detailed magnetic studies using a SQUID magnetometer as well as EPR spectroscopy are under investigation.

Conclusion

We generated a new series of Mn−dicarboxylate compounds, MnDC-*n*, which contain tunable interlayer distances using various α,*ω*-dicarboxylic acids by hydrothermal synthesis. The single-crystal analyses for MnDC-*n* (*n* = 3 and 5) reveal that odd members present the same crystal symmetry and conformation of dicarboxylate ligand, which is different from MnDC-*n* compounds of even members. The manganese−oxygen connectivities of both even and odd members of MnDC-*n* are very similar, and the resulting magnetic properties are predominantly ascribed to the Mn−O−Mn infinite chains and 2D canted antiferromagnetism. This series of compounds illustrates the possible synthesis of metal dicarboxylates extended to other transition metal ions which could exhibit magnetic anisotropy.

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