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Hydrothermal Synthesis and Magnetic Behavior of a Novel Layered Coordination Polymer Generated from Manganese(II) Adipate

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A novel, two-dimensional organic/inorganic coordinate polymers, $Mn_2(H_2O)[O_2C(CH_2)_4CO_2]_2$, was synthesized as single crystals by the hydrothermal reaction of $MnCl_2$ with adipic acid in the presence of base and characterized by single-crystal X-ray diffraction, infrared spectroscopy, thermal analysis, and SQUID magnetic measurement. It crystallized in the monoclinic space group $C2/c$(No. 15), with $a = 21.671(2)$ Å, $b = 7.6023(7)$ Å, $c = 9.1452(9)$ Å, $\beta = 108.849(7)$ Å, $Z = 4$. The title compound presents a structure constituted by the stacking along [100] of MnO_6 layers interleaved with adipate ions. The novel feature of the anionic layer is that it contains close-packed trans alkyl chains residing in an extended framework. Magnetization measurement shows this compound is antiferromagnetic below 15 K.

Introduction

The design of new solid-state architectures has recently driven much attention and increasing interests.[1] Advanced crystal engineering by selecting structural ligands and the coordination geometry of transition metal ions as a building block may give a series of novel inorganic frameworks with various interesting crystal structures.

Among a number of ligands employed as building blocks, the two end functional groups of α,ω-diphosphonate,[2] carboxyphosphonate,[3] and dicarboxylate[4−6] ligands could yield a variety of crystal structures of coordination complex even in similar chemical formulas depending on conformation of carbon chains and end functional groups. Those compounds are characterized as organic/inorganic hybrids with pillared layer structure assembled from the molecular precursors in solution. Recently, McCann et al. reported the syntheses and X-ray crystal structures of transition metal complexes containing the saturated α,ω-dicarboxylate and their derivatives[5] prepared in ambient condition. They have used transition metal dicarboxylates as precursors to prepare extended inorganic solids. The increased activity in the field of metal di- and tricarboxylates [4,7] is primarily due to the wide variety of structures that can be introduced by the appropriate choice of organic moiety covalently bound to the metal cation−carboxylate anion network. In general, the transition metal dicarboxylates prepared under ambient condition give usually complicated solid-state phases with various hydrate water contents. For instance, most of manganese dicarboxylates prepared under ambient pressure are undoubtedly related to crystal structure of the polymeric tetraaqua complex $\{Ni(O_2C(CH_2)_4CO_2)(H_2O)_4\}_n$, in which the octahedral nickel(II) atom is coordinated by four water molecules and a single carboxylic oxygen atom from two different *transoid* diacidic ligands.[6] In the latter species single carboxylate oxygen from the opposite ends of the diacidic ligands is joined to a neighboring nickel center, thus generating a polymeric chain.

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However, hydrothermal reaction enhances metal–ligand interactions rather than metal–water coordination, and finally this method could produce three-dimensional networks as clearly demonstrated in several dicarboxylate compounds.[4] This dramatic change of crystal structure was also observed in the coordination solids of manganese(II) 1,3,5-benzenetricarboxylate hydrate and anhydrous.[7] The hydrothermal synthesis of inorganic compounds is not only a common technique for the preparation of oxides such as zeolites[8] and metal phosphates,[9] but also a very promising route to new extended coordination solids since the nature and temperature of the hydrothermal fluid can be varied over a wide range.[10] Under hydrothermal conditions, carboxylic ligand is part of the framework leading to the formation of neutral network, which results in hybrid open networks with various molecules depending on the size of template ions.

There is a large volume of literature on two-dimensional amphiphilic layered structures, specially on the well-known layered crystals of organic–inorganic compounds such as alkylzirconium phosphates and phosphonates,[1k,11] $Zr(O_3POR)_2$ and $Zr(O_3PR)_2$, respectively, as well as the microcrystalline polymers of *n*-alkylsiloxanes from the hydrolysis of *n*-octadecyltrichlorosilane.[11] We note all these compounds consist of bilayered stacks of highly trans alkyl chains, in which the interior of bilayer exhibits a translational chain ordering. Some pillared layered structures[2,3] have been reported by use of two end functional ligands, but the interlayer alkyl chains are less dense compared to bilayer organic–inorganic compounds.

On the contrary, to our knowledge, a topology of well-aligned, closed packed alkyl chains of medium length such as six carbons in our study, has not been reported in the infinite hybrid network with two-dimensional inorganic metal–oxygen layers cross-linked. In this paper, we present here the synthesis of $Mn_2(H_2O)[O_2C(CH_2)_4CO_2]_2$ (**1**), a new manganese carboxylate with a two-dimensional array of edge and corner sharing $Mn(II)O_6$ interconnected by adipate bidentate anions. This compound has been fully characterized by FT-IR spectroscopy, microanalysis, thermal analysis, powder, and X-ray single crystal diffraction, and magnetic susceptibility measurements. Unlike previously reported metal dicarboxylates, this compound has no open framework but assembled organic layer and unique manganese site in the crystal structure.

Experimental Section

Manganese(II) chloride tetrahydrate(99.99%), adipic acid(99%) and potassium hydroxide(99.99%) were used as received from Aldrich. Thermogravimetric analysis (TG) were conducted on a TA instruments SDT 2960 simultaneous TG in a nitrogen atmosphere using a heating rate of 5 °C/min from room temperature to 1000 °C. Powder X-ray diffraction was performed on a Rigaku 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 sample was ground with dry KBr and pressed into a transparent disk. 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 of **1**. Measured susceptibility data were corrected for the contribution of the sample holder. Elemental analysis was performed by the Inter-University Center of Natural Science Research Facilities in Seoul National University.

Table 1. Crystal Data of $Mn_2(H_2O)[O_2C(CH_2)_4CO_2]_2$

empirical formula	$Mn_2C_{12}H_{18}O_9$
fw	416.15
space group	$C2/c$ (No. 15)
unit cell dimens	$a = 21.671(2)$ Å $b = 7.6023(7)$ Å $c = 9.1452(9)$ Å $\beta = 108.849(7)°$
vol	1425.9(2) Å^3
Z	4
calcd density	1.938 g cm^{-3}
measd temp	297(2) K
wavelength	0.71073 Å
abs coeff	1.818 mm^{-1}
final R indices ($I > 2\sigma(I)$)	R1$^a = 0.0380$, wR2$^b = 0.1012$

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = [\sum|w(F_o^2 - F_c^2)^2|/\sum|w(F_o^2)^2|]^{1/2}$, $w = [\sigma(F)]^{-1}$.

Synthesis of 1. A mixture of 0.49 g (2.5 mmol) of $MnCl_2{\cdot}4H_2O$, 0.73 g (5.0 mmol) of adipic acid, and 0.66 g (11.8 mmol) of KOH with $MnCl_2$:adipic acid:KOH ratio of 1:2.0:4.7(pH = 5.3) was heated along with 10 mL of water in a 23 mL capacity Teflon-lined reaction vessel at 180 °C for 4 days and then cooled to room temperature by quenching in cold water bath. About 0.35 g of **1** was obtained as colorless (slightly pale-red) platelike crystals after washing with water. Remaining adipic acid was leached out with acetone. The isolated product gave approximately 65% yield based on the $MnCl_2$. The formation of a little amount of black chunky crystals such as Mn_3O_4 strongly depends on the initial pH and the ratio of starting materials though the byproduct could be easily isolated manually under optical microscope by handpicking. After a number of experiments we could find the reaction condition that gave only expected compound **1** as described above. The identity of the collected $Mn_2(H_2O)[O_2C(CH_2)_4CO_2]_2$ sample for various characterization was confirmed by matching the powder diffraction pattern to that calculated from the single-crystal structure. Anal. Calcd: Mn, 26.43; C, 34.60; H, 4.32. Found: Mn, 25.79; C, 34.33; H, 4.25. The infrared spectra exhibited the following absorption (KBr pellet): 3500–3100 (s, v br), 2934 (s), 2867 (w), 1571 (vs), 1398 (vs), 1319 (m), 1271 (m), 1076 (m), 804 (m), 738 (m), 658 (s), 540 (m) cm^{-1}. The low-frequency shift of ν_{asym}(OCO) peak in 1571 cm^{-1} reveals the absence of free adipic acid and confirms the complete coordination with manganese ion.

X-ray Structure Analysis. Single-crystal X-ray data were collected on a Siemens P4 automated four-circle diffractometer equipped with graphite monochromated Mo $K\sigma$ radiation ($\lambda = 0.71079$ Å). A crystal of dimensions $0.4 \times 0.76 \times 0.04$ mm^3 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 a monoclinic unit cell similar to the final crystallographic results. Data collections were performed with a θ 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 based on ϕ-scan data of six averaged reflections. Compound **1** crystallized in the monoclinic crystal system. The pattern of systematic absences observed in the data was consistent with either the space group $C2/c$ or Cc. The centric space group $C2/c$ was assumed and confirmed by the successful solution and refinement of the structure.

A summary of crystal data is represented in Table 1. The structure was solved by direct methods (SHELX-86)[12] and standard difference Fourier techniques (SHELX-97).[13] Manganese and oxygen atoms were

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Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters[a] for Non-Hydrogen Atoms

atom	x	y	z	U_{eq}
Mn	0.521957(14)	0.29604(4)	0.95953(4)	0.0123(2)
O(1)	0.43024(9)	0.1992(2)	0.9744(2)	0.0213(5)
O(2w)	0.5000	0.0961(3)	0.7500	0.0174(5)
O(3)	0.57264(8)	0.0795(2)	1.1031(2)	0.0169(4)
O(4)	0.59589(8)	0.3871(2)	0.8712(2)	0.0174(4)
O(5)	0.45604(7)	0.5192(2)	0.8514(2)	0.0148(4)
C(1)	0.40512(10)	0.0495(3)	0.9544(2)	0.0132(5)
C(2)	0.34318(11)	0.0206(3)	0.9942(3)	0.0178(5)
C(3)	0.28278(11)	0.0506(3)	0.8529(3)	0.0187(5)
C(4)	0.21967(11)	0.0123(3)	0.8861(3)	0.0186(6)
C(5)	0.15935(11)	0.0482(3)	0.7475(3)	0.0176(5)
C(6)	0.59575(10)	0.4816(3)	0.7600(3)	0.0123(5)

[a] The manganese, oxygen, carbon(except hydrogen) atoms were refined anisotropically and are given in the form of the equivalent displacement parameter defined as $U_{eq} = {}^1/_3\Sigma_i\Sigma_j U_{ij}a_i{}^*a_{ij}{}^*$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $Mn_2(H_2O)[O_2C(CH_2)_4CO_2]_2$

Mn−O(1)	2.165(2)	O(4)−Mn−O(5)[a]	95.38(6)
Mn−O(2w)	2.370(2)	O(4)−Mn−O(1)	162.37(7)
Mn−O(3)	2.170(2)	O(5)[a] −Mn−O(1)	98.08(7)
Mn−O(4)	2.130(2)	O(4)−Mn−O(3)	100.40(6)
Mn−O(5)[a]	2.158(2)	O(5)[a] −Mn−O(3)	94.09(6)
Mn−O(5)	2.232(2)	O(1)−Mn−O(3)	89.96(7)
		O(4)−Mn−O(5)	92.13(6)
O(1)−C(1)−O(3)[c]	123.7(2)	O(5)−Mn−O(5)[a]	78.73(6)
O(4)−C(6)−O(5)[b]	123.3(2)	O(1)−Mn−O(5)	79.46(6)
		O(3)−Mn−O(5)	166.14(7)
C(1)−O(1)−Mn	131.8(2)	O(4)−Mn−O(2w)	83.16(5)
C(1)[c]−O(3)−Mn	121.15(14)	O(5)[a] −Mn−O(2w)	178.54(5)
		O(1)−Mn−O(2w)	83.36(5)
Mn−O(2w)−Mn[b]	100.25(9)	O(3)−Mn−O(2w)	86.15(6)
Mn−O(5)−Mn[a]	101.27(6)	O(5)−Mn−O(2w)	101.33(6)

[a] Symmetry transformation used to generate equivalent atoms: $-x+1$, $-y+1$, $-z+2$. [b] Symmetry transformation used to generate equivalent atoms: $-x+1$, y, $-z+{}^3/_2$. [c] Symmetry transformation used to generate equivalent atoms: $-x+1$, $-y$, $-z+2$.

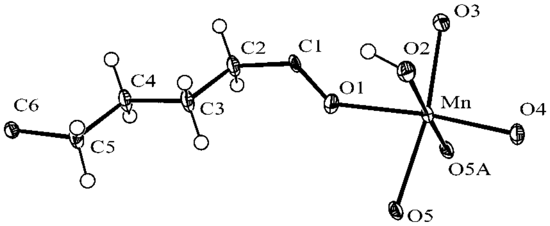

Figure 1. View of $\{Mn(H_2O)_{1/2}(O_2C(CH_2)_4CO_2)\}$ unit of **1**. Thermal ellipsoids are shown at 50% probability.

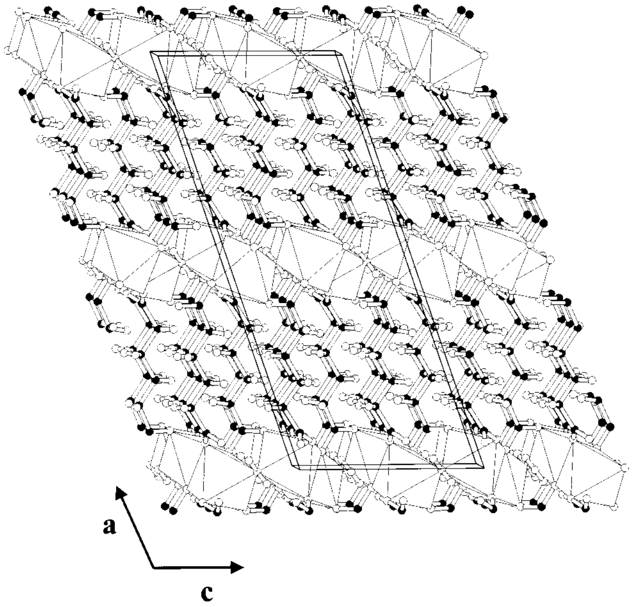

Figure 2. Views of the framework along the [010] direction. Polyhedra represent the MnO_6 octahedra and black sphere corresponds to carbon atoms. Oxygen of water molecule locates between two MnO_6 polyhedra in the same plane.

first located and the carbon atoms were found by difference Fourier maps. All hydrogen atoms attached to carbons positions program generated and included in the refinements as a riding model. The hydrogen on water molecule was refined separately according to electron density difference. Absorption corrections were applied using the SHELX-86 program. Refinements for 110 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 reliability factors converged to $R1(F_o) = 0.0380$ and $wR2(F_o^2) = 0.1012$. Fractional atomic coordinates are given in Table 2 and selected bond distances and angles in Table 3.

Results and Discussion

Synthesis. Hydrothermal treatment of Mn−adipate in an aqueous solution gives **1** in high yield. Especially, the reaction temperature and initial pH value of the solution are very critical to obtain the title compound. Small decrease of hydroxide concentration gives extraction of adipic acid after the hydrothermal treatment. Various alkali metal−hydroxide have been used to synthesis and yield the same compound when the solution pH is similar. Reaction time is likely to control only crystallinity and crystal size of product. Crystal of **1** gives the rectangular platelike appearance. Each sheet is a single crystal having two dimensions, presumably perpendicular to *a* axis, due to alternative stacking of amphiphilic layers in the crystal structure of **1**. The powder X-ray diffraction pattern supports the preferred crystal growth along *bc* plane since (200) peak is strongly enhanced compared with other (*hkl*) ones according to the intensity calculation. The other transition metal adipates with the same crystal structure such as iron(II)−adipate, $Fe_2(H_2O)[O_2C(CH_2)_4CO_2]_2$, have been also successfully synthesized by similar synthetic condition.[14]

Crystal Structure Determination. Figure 1 shows $\{Mn(H_2O)_{1/2}(O_2C(CH_2)_4CO_2)\}$ unit which provides the fundamental structural motifs in the design of the two-dimensional Mn−O framework of **1**. The structure of **1** is understood as two-dimensional layered structure, consisting of chains of edge-sharing MnO_6 polyhedra, along the [010] and [001] direction, linked together by carboxylate groups along the [001] direction. The complex connection schematized in Figure 2, involves the formation of MnO_6 layer with assembled alkyl chains along [100] direction. The hydrophobic characteristic of alkyl chains induces self-assembly of organic moiety leading to the complete packing of *intra*, and *inter*layer spaces. The organic and inorganic layers are stacked along *a* axis [perpendicular to (100) plane], the length of which is the interlayer spacing of 10.25 Å. It is worth pointing out that adipate ligands have the terminal groups rotated by 90° with respect to one another. All adipate are located along *a* axis and surrounded six other chains with

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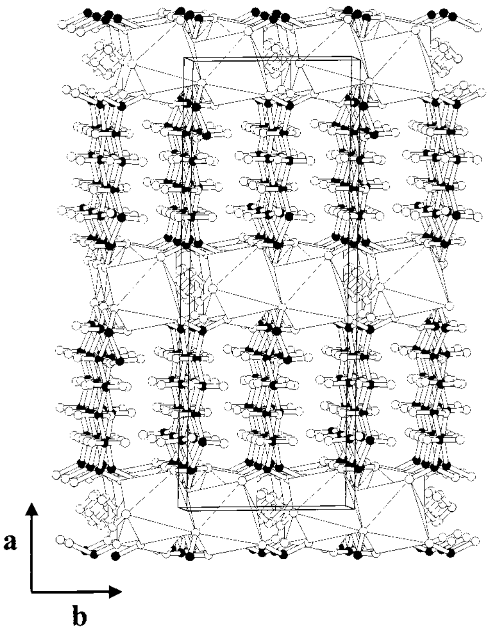

Figure 3. Projection of the structure of **1** along the [001] direction showing the linkage of the chains of manganese polyhedra by the carbon chains (in black) along the [100] direction.

regular distance. Their alkyl chain has trans conformation with the *inter*chain distance of about 4.1 Å, a value quite close to the chain-chain spacings observed in dense solid phases of alkyl-chains, such as high surface pressure Langmuir monolayers of saturated alkyl-chain amphiphiles[15] and crystalline *n*-alkanes.[16] The hydrophobic characteristic of alkyl-chains is ascribed to driving force to induce self-assembly of organic moiety leading to the complete packing of *intra*- and *inter*layer spaces. The dicarboxylate complexes with longer chains could be synthesized in the appropriate solvothermal condition due to low solubility in aqueous solution, which is now under investigation. It should be noted that this class of layered structure is model system mimicking the two-dimensional infinite metal-oxide or metal-hydroxide compounds with large interlayer expansion similar to intercalation reactions.

Manganese atoms occupy only one crystallographic site with an octahedral coordination of oxygen atoms arising from the five adipate ions and one water molecule. The carboxylate groups which ensure the linkage between upper and down MnO_6 layers along [100] direction, also chelates two neighboring octahedra in a MnO_6 layer, as shown in Figure 3. Edge-shared octahedra, $[Mn_2O_8^{12-}]$, share only vertex (O(2*w*)) of water molecule in MnO_6 layer, consisting of thin hydrophilic layer between thick hydrophobic crystalline alkyl-chain overlays. Each carboxylate group has covalent bonds with three different manganese atoms and an adipate ligand binds six manganese ion between the layers, in which O(3) has a terminal Mn−O bond, O(5) form Mn−μ_2−O bridging bonds.

Figure 4 shows a portion of **1**, the layer of MnO_6 octahedra, illustrating the details of the MnO_6 linkage. The metal oxide framework can be described as an infinite zigzag chains of edge-sharing two manganese octahedra linking with oxygen atom of water through corner sharing. All Mn atoms are six coordinate and MnO_6 octahedra are strongly distorted with four short

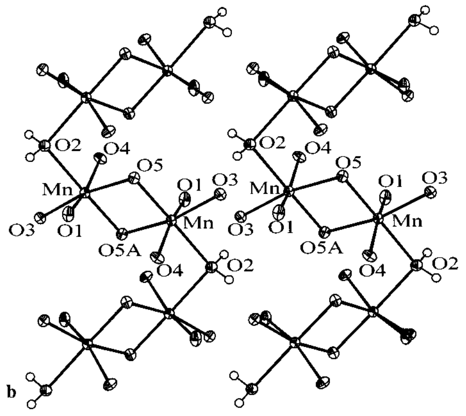

Figure 4. Structure showing the connectivity within a single layer of *bc* plane including the numbering scheme used in Table 2. The atoms are drawn with 50% probability ellipsoids.

Mn−O bond distances (2.130(2)−2.170(2) Å), two long (2.232(2) and 2.370(2) Å). The oxygen atom of water, O(2w), is shared between two manganese atoms with Mn−μ_2−O(H_2) bonds, which show largest Mn−O bond length. We assign O(2*w*) as Mn−μ_2−O(H_2) rather than μ_2-oxo or −OH since H is within hydrogen bonding distance to O(3) of a nearby carboxylate, and results in a charge-balanced compound, and has a bond valence sums of 0.42(excluding the hydrogen) while the calculated valence sums[17] for other oxygens range from 1.71 to 2.02. The coordinated water formulation is also consistent with TGA behavior (vide infra) and the appearance of broad O−H stretches in the IR spectra. Only that noticeable hydrogen bond linkage exists in the crystal structure, a bond between the hydrogen atom of the water and an oxygen atom of neighboring octahedron. The O−H bond distances of [O(2*w*)−H(O2*w*)−O(3)] linkage 0.93 and 1.84 Å, respectively. Trans bond angles around Mn centers range from 162.37(7) to 178.54(5)°, and cis angles vary from 78.73(6) to 101.33(6)°. The Mn···Mn separations in the structure are 3.40 and 3.64 Å in the edge-shared and in the corner shared bioctahedra, respectively. None of these distances is sufficiently short to imply any metal−metal bonding. All bond distances within the adipate ligands are typical.

Thermal Analysis. Figure 5 show the result of thermogravimetric analysis performed on **1** in a nitrogen atmosphere. Two distinct mass loss regions around 210 and 260 °C, are seen in TGA of the title compound (Figure 5a). The first mass loss at 210 °C is due to dehydration of coordinate H_2O. The temperature of dehydration for **1** is similar to that for the $Mn(H_2O)[O_2C(CH_2)_4CO_2]$ sample prepared under ambient pressure.[18] It is presumably expected that this occur above the boiling point of water attributed to the coordination with manganese ion in the crystal lattice. The observed mass loss of 4.7% corresponds to 1.1 equiv of H_2O per formula unit. Interestingly, water is irreversibly diffusing out of the compound as shown in the Figure 5b, and the repeated thermal analyses confirmed that the rehydration in ambient condition does not occur even in a week. The crystallinity becomes poor after dehydration at 250 °C, which was confirmed by the powder X-ray diffraction spectra. With respect to crystal structure, evaporation of water would occur within the hydrophilic layer of *bc* plane leading to perturbation of two-dimensional layer in which water contributes the coordination between two manganese atoms. The next mass loss(260 °C) corresponds to loss of coordinated

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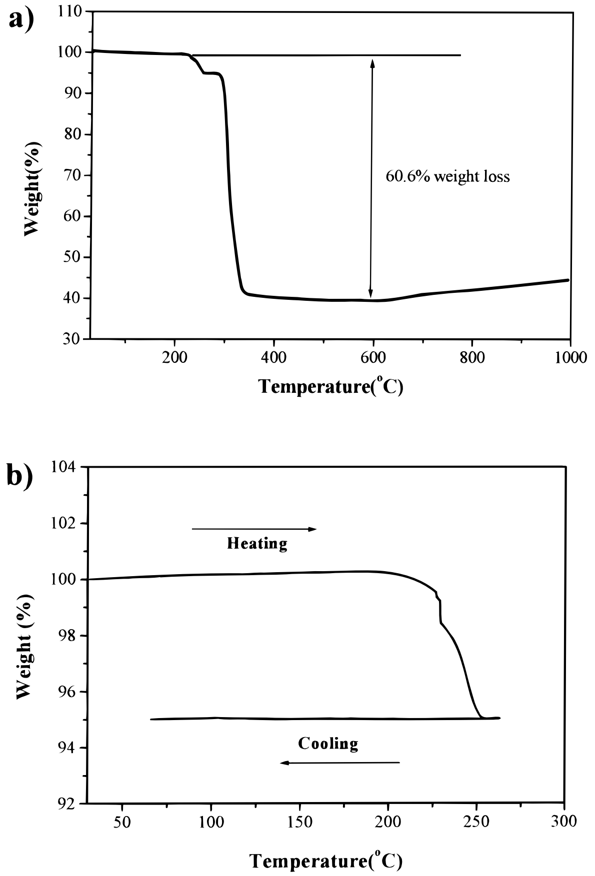

Figure 5. Thermogravimetric analysis results for **1** for (a) room temperature to 1000 °C (a) and for the (b) programmed thermal cycle up to 250 °C.

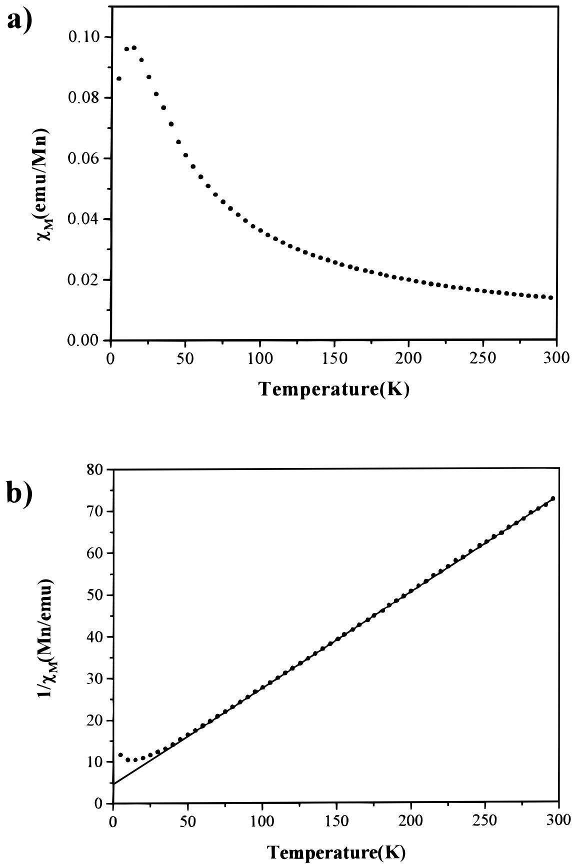

Figure 6. (a) Magnetic susceptibility(per manganese ion) vs temperature plot for **1**. (b) Inverse magnetic susceptibility(per manganese ion) vs temperature plot for **1**: (●) experimental data; (—) best fit to the Curie−Weiss law for data of 35−300 K.

adipate, giving MnO and carbon.[18] The observed remained weight percent of 39.4% (at ca. 600 °C) approximates 39.9 wt % of the expected value for MnO and equivalent elementary carbon. We attribute the slight mass increase at the highest temperatures to easy conversion of MnO to Mn_3O_4 via adventitious oxygen. The powder X-ray diffraction spectra for the products after 1000 °C heat treatment in the TGA was indexed to Mn_3O_4 and small amount of unidentified manganese oxide phases.

Magnetic Measurements. The presence of infinite chain of edge and corner sharing MnO_6 is attributed to important magnetic properties of the compound, with the predictable existence of strong magnetic couplings between $3d^5$ magnetic centers. The temperature dependence of inverse magnetic susceptibility for the compound, measured with a SQUID magnetometer in 100 G shows simple Curie−Weiss paramagnetic behavior from 35 to 300 K (Figure 6). The best linear fit of $\chi^{-1}(T)$ data above 35 K yields $C = 4.37$ emu Mn mol^{-1}, and $\theta = -5$K. The high spin d^5 electronic configuration is isotropic in the perfect octahedral crystal field. The room-temperature effective magnetic moment (μ_{eff}) is 5.74μ_B per mole of manganese, which is generally observed in high-spin Mn(II)($3d^5$) centers(5.65−6.10)[19] and is close to 5.77μ_B, the value reported for $Mn(O_2C(CH_2)_4CO_2)\cdot H_2O$ polycrystalline.[5a] This is also in agreement with bond valence calculation[17] which give 2.05(2). Around 15 K, a marked change in the $\chi^{-1}(T)$ curve, characterized by an important decrease of susceptibility, indicates an antiferromagnetic behavior. The antiferromagnetism of the title compound can be understood from structural considerations and superexchange mechanism.[20] Since all of manganese atoms have same crystallographic position and are surrounded by two manganese atoms in which manganese octahedra is linked by corners and shares edges with neighboring MnO_6 octahedra as shown in Figure 4. The layer is composed of the zigzag chains along the [001] direction and Mn−O−Mn connection of different chain is separated with each other. In terms of superexchange magnetic couplings, this structure exhibits 90° interactions through two different Mn−O−Mn of O(2*w*) and O(5) oxygen atoms. The atomic positions give the values of the different superexchange angels for the title compound, 100.25(9)° [Mn−O(2*w*)−Mn] and 101.27(6)° [Mn−O(5)−Mn]. If there is d^5−d^5 superexchange through 90° interactions, it can be antiferromagnetic as illustrated for instance by $Mn(CH_3COO)_2\cdot 4H_2O$ possessing trimmeric manganese(II) units.[21] The neutron diffraction work[21b] for the manganese acetate shows that the interaction within the Mn−O−Mn−O−Mn groups is antiferromagnetic and relatively large compared to the coupling between the trimeric units in the same plane or between planes. In our case, the value of θ(−5K) indicates moderate antiferromagnetic interactions. If all the interactions, whatever the superexchange angle, were antiferromagnetic, a large value of θ would be expected. In addition, the magnetic coupling in the linking MnO_6 chain along [001] direction but the long-range interaction between chains is not clear. The

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neutron diffraction study for the compound **1** in magnetically ordered temperature region is now in progress to determine the spin arrangement in the crystal structure of **1**.

In conclusion, a new layered manganese adipate compound was synthesized as a single phase by hydrothermal method and was determined by single-crystal X-ray diffraction. We found that the reaction parameters such as temperature, concentration, and initial pH are critical for successful synthesis. The structure of this compound can be characterized as a single layer of MnO_6 polyhedra chains separated by close packed crystalline alkyl chains. This work illustrates the possibility of synthesis of new layered metal dicarboxylates, by self-assembly from the molecular precursors. Studies are in progress to increase the length of the organic chain and vary the divalent transition metals in octahedral sites by similar reaction conditions.

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Supporting Information Available: X-ray crystallographic file, in CIF format, for the structural determination of $Mn_2(H_2O)[O_2C(CH_2)_4CO_2]_2$ (**1**). This material is available free of charge via the Internet at http://pubs.acs.org.

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