Inorg. Chem. **2000,** *39,* 4169−4173

Three-Dimensional Manganese(II) Coordination Polymers Based on *m*-Pyridinecarboxylates: Synthesis, X-ray Structures, and Magnetic Properties

Wenbin Lin,*[†,‡] Mary E. Chapman,[†]
Zhiyong Wang,[†] and Gordon T. Yee*[§]

Department of Chemistry, Brandeis University,
Waltham, Massachusetts 02454, and
Department of Chemistry and Biochemistry,
University of Colorado, Boulder, Colorado 80309

Received February 29, 2000

Introduction

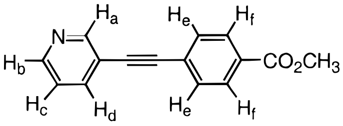
Strong metal−ligand coordination bonds and their directionality have recently been extensively exploited for the design and synthesis of extended solid materials.[1−7] Compared to metal oxides and other simple inorganic solids, the structural diversity of polymeric coordination networks can be enormous owing to the ability to incorporate a vast number of organic ligands into the frameworks. The prospect of tuning the properties of metal−organic frameworks via a systematic change of the organic linking ligands provides further impetus for the research on metal−organic frameworks.[8−11] Our recent preliminary results on the tuning of nonlinear optical properties of coordination networks by incorporating organic linking ligands of different length (hence conjugation) illustrate the potential of such a rational synthetic approach.[12−14] However, due to the presence of many subtle interactions in such supramolecular systems, the construction of extended solids based on metal−organic coordination networks is still at a primitive stage and lacks predictability.[15] The detailed knowledge of such interactions on metal−organic coordination networks can be obtained by systematically changing the organic bridging ligands (building blocks). Our work focuses on the construction of coordination networks by using bridging ligands with the same geometry but different length, in particular conjugated π-systems.[12−14,16] Such ligands have rigid conformations and will therefore simplify the crystal engineering of the resulting coordination networks. Herein we wish to report the synthesis, X-ray structures, and magnetic properties of two topologically similar 3-D manganese(II) coordination polymers based on bridging *m*-pyridinecarboxylate: bis(nicotinato)manganese and bis[4-(3-pyridyl)ethynylbenzoato]manganese.

Experimental Section

Materials and Methods. 3-Bromopyridine was purchased from Alfa/AESAR, and all other chemicals were purchased from Aldrich Chemical Co. 3-Ethynylpyridine was synthesized according to the published procedure.[17] The IR spectra were recorded as KBr pellets on a Paragon 1000 FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were taken on a Varian Unity-Plus 400 spectrometer. Thermogravimetric analyses were performed under nitrogen at a scan speed of 10 °C/min on a Shimadzu TGA-50 TG analyzer.

Magnetization vs temperature data was obtained on a Quantum Design MPMS-7 SQUID magnetometer in a 100 G applied field. Approximately 20 mg of **1** and 10 mg of **2** were loaded between two cotton plugs in gelatin capsules. Diamagnetic corrections for the samples were calculated from Pascal's constants. The correction for the capsule and the cotton was calculated from the measured average gram susceptibility of several nominally identical empty capsules and cotton plugs.

Synthesis of Methyl 4-(3-Pyridyl)ethynylbenzoate. A mixture of 3-ethynylpyridine (1.03 g, 10 mmol) and methyl 4-bromobenzoate (2.02 g, 10 mmol) in 50 mL of diethylamine was refluxed in the presence of bis(triphenylphosphine)palladium dichloride (40 mg, 0.06 mmol) and copper(I) iodide (10 mg, 0.05 mmol) for 20 h. Diethylamine was removed by evaporation under reduced pressure, and the residue was dissolved in 50 mL of ethyl acetate and extracted twice with 50 mL of water. The organic layer was dried over $MgSO_4$ and evaporated to dryness. Silica gel column chromatography eluting with a mixture of hexane and ethyl acetate (2:1 v/v) afforded 2.23 g of pure product (67% yield). Mp: 141−143 °C. ^{1}H: δ 8.78 (br s, 1H, H_a), 8.58 (br d, 1H, $J = 4.8$ Hz, H_b), 8.04 (d, 2H, $J = 8.8$ Hz, H_f), 7.83 (dt, 1H, $J_1 = 7.6$ Hz, $J_2 = 2.0$ Hz, H_d), 7.60 (d, 2H, $J = 8.8$ Hz, H_e), 7.31 (dd, 1 H, $J_1 = 7.6$ Hz, $J_2 = 4.8$ Hz, H_c), 3.93 (s, 3H, CH_3). ^{13}C{^{1}H}: δ 166.4, 152.2, 148.9, 138.6, 131.6, 130.0, 129.6, 127.1, 123.1, 120.0, 91.8, 88.6, 52.3.



Synthesis of Bis(nicotinato)manganese(II), 1. A mixture of $Mn(ClO_4)_2 \cdot 6H_2O$ (0.181 g, 0.5 mmol) and 3-cyanopyridine (0.111 g, 1.0 mmol) was thoroughly mixed with ethanol (0.07 mL), water (0.3 mL), and pyridine (0.12 mL) in a heavy-walled Pyrex tube. The tube was frozen under liquid nitrogen, sealed, and heated inside an oven at 110 °C. After 1 week of heating, the tube was opened, and pale yellow crystals were obtained. The product was washed with 1 mL of ethanol three times. Yield: 128 mg (88%). Anal. Calcd for $MnC_{12}H_8N_2O_4$, **1**: C, 48.2; H, 2.70; N, 9.36. Found: C, 47.8; H, 2.78; N, 8.75. IR (cm^{-1}): 1664 (m), 1609 (s), 1571 (s), 1420 (w), 1400 (s), 1320 (w), 1193 (w), 1160 (w), 1115 (w), 1044 (m), 1032 (m), 840 (m), 754 (s),695 (m), 636 (m), 545 (w).

[†] Brandeis University.

[‡] E-mail: wlin@brandeis.edu.

[§] University of Colorado.

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10.1021/ic000227v CCC: $19.00

Table 1. Data for the X-ray Diffraction of **1** and **2**[a]

	1	**2**
chemical formula	$MnC_{12}H_8N_2O_4$	$MnC_{28}H_{16}N_2O_4$
fw	299.14	499.37
space group	*C*2/*c* (No. 15)	*C*2/*c* (No. 15)
Z	4	4
T, °C	−75(1)	−75(1)
λ(Mo Kα), Å	0.71073	0.71073
a, Å	14.918(1)	26.962(1)
b, Å	9.349(1)	10.100(1)
c, Å	8.805(1)	7.951(1)
β, deg	114.756(1)	93.393(2)
V, Å^3	1115.2(1)	2161.6(2)
ρ_{calc}, g/cm^3	1.78	1.53
μ, cm^{-1} (Mo Kα)	12.0	6.5
N_{ref} (total)	1331	2610
N_{ref} (obs), $I > 2\sigma(I)$	1289	1800
N_{par}	104	191
R1	0.025	0.064
wR2	0.073	0.128
goodness of fit	1.00	1.34
min and max residual density, e/Å^3	−0.45, 0.40	−0.46, 0.41

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $GOF = [\sum[w(F_o^2 - F_c^2)^2]/(\text{no. of reflections} - \text{no. of parameters})]^{1/2}$.

Synthesis of Bis[4-(3-pyridyl)ethynylbenzoato]manganese(II), 2. A mixture of $Mn(ClO_4)_2 \cdot 6H_2O$ (0.0904 g, 0.25 mmol) and methyl 4-(3-pyridyl)ethynylbenzoate (0.1107 g, 0.5 mmol) was thoroughly mixed with ethanol (0.11 mL), water (0.36 mL), and pyridine (0.14 mL) in a heavy-walled Pyrex tube. The tube was frozen under liquid nitrogen, sealed, and placed inside an oven at 96 °C. After 96 h of heating, colorless rectangular crystals were obtained. Yield: 110 mg (94%). IR (cm^{-1}): 1719 (w), 1648 (s), 1593 (s), 1544 (s), 1475 (w), 1414(s), 1401 (s), 1326 (w), 1282 (w), 1092 (w), 866 (w), 779 (m), 699 (m), 640 (w).

X-ray Data Collections and Structure Determinations. Data collection for **1** (**2**) was carried out with a colorless crystal of dimensions of 0.30 × 0.34 × 0.38 mm (0.05 × 0.15 × 0.30 mm) on a Siemens SMART system equipped with a CCD detector using Mo Kα radiation. Of the 1331 (2610) unique reflections measured, 1289 (1800) reflections with $I > 2\sigma(I)$ were used in structure solution and refinement for **1** (**2**). The structures were solved by direct methods and refined on F^2 by full-matrix least squares using anisotropic displacement parameters for all non-hydrogen atoms.[18] All of the hydrogen atoms in **1** and **2** were located by geometric placing. Final refinement gave an R1 = 0.025 (0.064), wR2 = 0.073 (0.128), and goodness of fit = 1.00 (1.34) for **1** (**2**). Experimental details for X-ray data collections of **1** and **2** are tabulated in Table 1, while selected bond distances and angles for **1** and **2** are listed in Table 2. All the drawings were made using either XP[18] or CAMERON[19] programs.

Results and Discussion

Synthesis. The ligand precursor methyl 4-(3-pyridyl)ethynylbenzoate was synthesized in 67% yield by a Heck coupling reaction[20] between 3-ethynylpyridine and methyl 4-bromobenzoate as illustrated in Scheme 1. Methyl 4-(3-pyridyl)ethynylbenzoate was characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for **1** and **2**

Mn1−O2	2.195(1)	Mn1−O2	2.186(2)
Mn1−O1B[a]	2.131(1)	Mn1−O1B	2.113(2)
Mn1−N1D	2.353(2)	Mn1−N1D	2.374(3)
O2−Mn1−O2A	165.44(4)	O2−Mn1−O2A	155.17(8)
O1B−Mn1−O2	100.27(4)	O1B−Mn1−O2	105.54(9)
O1C−Mn1−O2	90.34(4)	O1C−Mn1−O2	92.59(8)
O2−Mn1−N1D	84.83(4)	O2−Mn1−N1D	81.46(8)
O2A−Mn1−N1D	86.08(4)	O2A−Mn1−N1D	83.29(8)
O1B−Mn1−O1D	86.76(4)	O1B−Mn1−O1C	86.53(9)
O1B−Mn1−N1D	170.79(4)	O1B−Mn1−N1D	169.36(9)
O1C−Mn1−N1D	85.53(4)	O1C−Mn1−N1D	85.14(9)
N1D−Mn1−N1E	102.56(5)	N1D−Mn1−N1E	103.85(10)

[a] Symmetry Codes: A = $1 - x, y, {}^1/_2 - z$; B = $1 - x, 1 - y, -z$; C = $x, 1 - y, {}^1/_2 + z$; D = ${}^1/_2 - x, {}^1/_2 - y, -z$; E = ${}^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z$.

Bis(nicotinato)manganese, **1**, was obtained as large pale yellow crystals in 88% yield by a hydro(solvo)thermal reaction between $Mn(ClO_4)_2 \cdot 6H_2O$ and 3-cyanopyridine in a mixture of ethanol and water at 110 °C (Scheme 2). The IR spectrum of **1** exhibits peaks at 1571 and 1400 cm^{-1} that can be assigned to the antisymmetric and symmetric C=O stretches, respectively.[21] The nicotinate group in **1** has evidently resulted from the in situ hydrolysis of 3-cyanopyridine during the hydro(solvo)thermal synthesis.[12−14,16] Bulk purity of **1** was ensured via comparison of the XRPD pattern of **1** with a calculated XRPD pattern obtained from single-crystal reflection data.

Bis[4-(3-pyridyl)ethynylbenzoato]manganese(II), **2**, was obtained similarly by a hydro(solvo)thermal reaction between $Mn(ClO_4)_2 \cdot 6H_2O$ and methyl 4-(3-pyridyl)ethynylbenzoate (Scheme 2).[22] The structure of **2** can be inferred from the IR spectrum showing strong peaks at 1544 and 1401 cm^{-1} which are characteristic of carboxylate groups.

Single-Crystal X-ray Structures. Compound **1** crystallizes in the monoclinic space group *C*2/*c*. The asymmetric unit of **1** consists of one manganese atom and one nicotinate group with the Mn(II) center lying on a 2-fold axis. Each Mn(II) center is coordinated to four carboxylate oxygen atoms from four different nicotinate groups and to two pyridyl nitrogen atoms of two other nicotinate groups (Figure 1a). The geometry around the Mn(II) center can be best described as a slightly distorted octahedron, and the two pyridyl nitrogen atoms are cis to each other. The bond angles around the central Mn1 atom and the cis ligands range from 84.8° to 102.5°. The Mn1−O distances are 2.131(1) and 2.195(1) Å while the Mn1−N distance is 2.353(2) Å.

The X-ray single-crystal structure determination also reveals a complicated 3-D polymeric structure of **1**. First, adjacent Mn(II) centers are doubly bridged by the carboxylate groups of the nicotinate ligands to form an infinite zigzag chain structure (Figure 2a). All of the carboxylate bridges in the chain adopt a syn-syn conformation with a Mn−Mn distance of 4.91 Å. Second, each infinite zigzag Mn(nicotinate)$_2$ chain is connected to four adjacent chains via the ring systems of the nicotinate group to form a complex 3-D coordination polymer (Figure 3). The shortest Mn−Mn separations between adjacent chains are 7.33 and 8.80 Å for the Mn atoms that are cis and trans to the coordinated 3-pyridyl nitrogen atom, respectively. No significant $\pi-\pi$ interactions are observed in **1**; the shortest centroid-to-centroid distance for the adjacent pyridyl rings (of the nicotinate groups) is 4.49 Å.

Compound **2** also crystallizes in the monoclinic space group *C*2/*c* with one Mn atom and one (3-pyridyl)ethynylbenzoate

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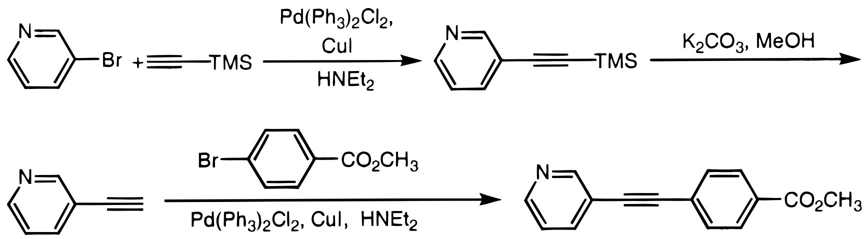
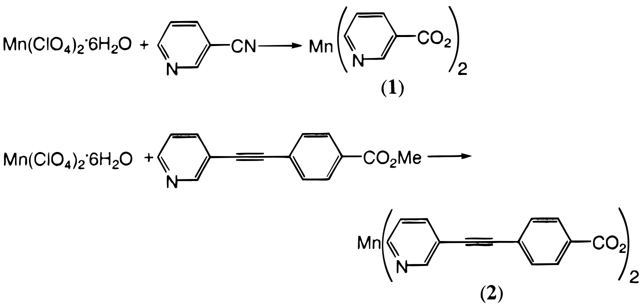
(22) Compound **2** can also be prepared by reacting $Mn(ClO_4)_2 \cdot 6H_2O$ and 4-(3-pyridyl)ethynylbenzonitrile under similar conditions.

Scheme 1



ligand in the asymmetric unit. As before, the Mn1 center in **2** lies on a 2-fold axis. The Mn(II) center in **2** is coordinated to four carboxylate oxygen atoms from four different (3-pyridyl)ethynylbenzoate groups and to two pyridyl nitrogen atoms of two other (3-pyridyl)ethynylbenzoate groups in a cis fashion (Figure 1b). The octahedral coordination environment of Mn1 in **2** is slightly more distorted than that of **1** with the bond angles around the central Mn1 atom and the cis ligands ranging from 81.5° to 105.5°. The Mn1–O and Mn1–N distances in **2** are very similar to those of **1**; the Mn1–O distances are 2.113(2) and 2.186(2) Å while the Mn1–N1 distance is 2.374(3) Å.

Scheme 2



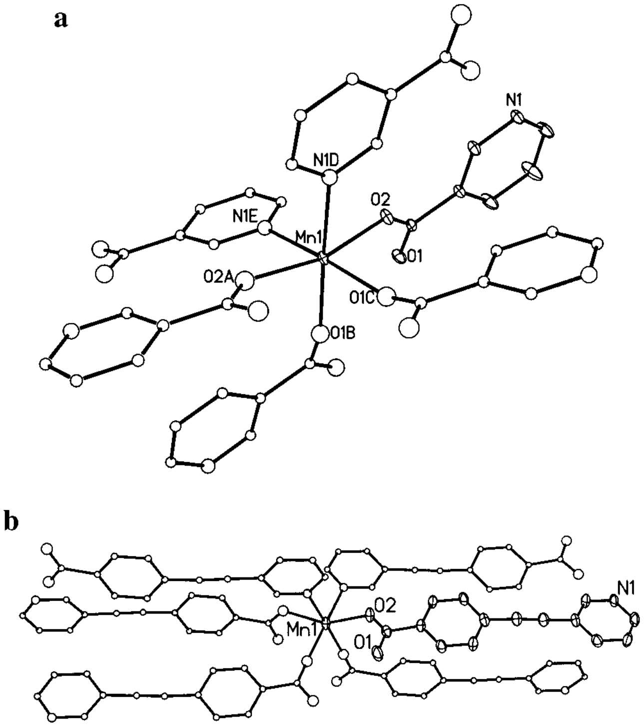


Figure 1. (a) Coordination environment in **1**. (b) Coordination environment in **2**. The asymmetric units are shown in ellipsoids at 30% probability. The circles with increasing sizes represent C, N, and O, respectively. Hydrogen atoms have been omitted for clarity.

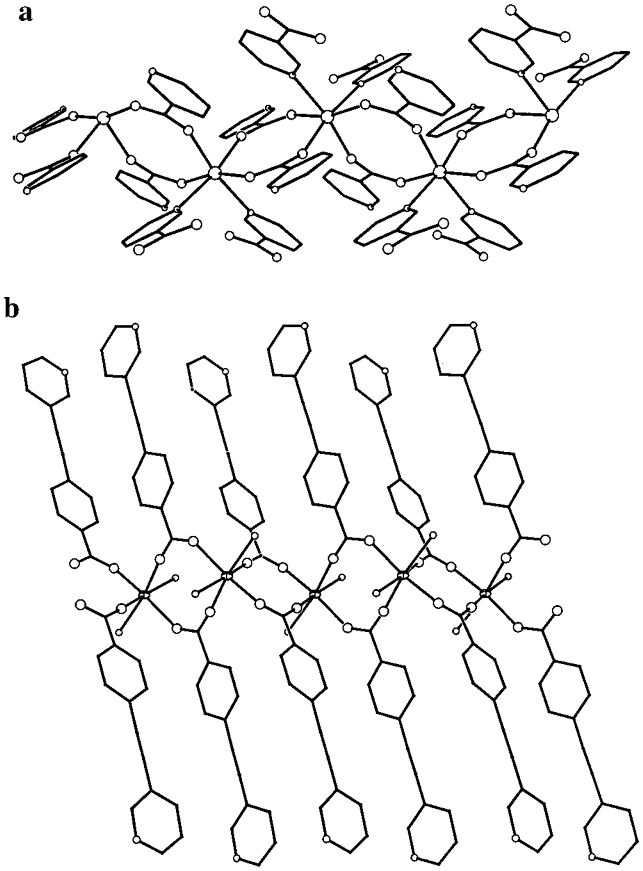


Figure 2. Views of the doubly carboxylate bridged Mn–Mn chains in **1** (a) and **2** (b). For clarity, the (3-pyridyl)ethynylbenzoate bridging ligands that use pyridyl nitrogen to coordinate to Mn(II) centers in **2** have been omitted (except pyridyl nitrogen atoms).

Interestingly, compounds **1** and **2** exhibit remarkably similar topologies in spite of the very different lengths of the nicotinate and (3-pyridyl)ethynylbenzoate bridging ligands. Mn(II) centers in **2** are doubly bridged by the carboxylate groups of the (3-pyridyl)ethynylbenzoate ligands to form an infinite zigzag chain structure very similar to that of **1** (Figure 2b). All of the carboxylate bridges in the chain also adopt a syn-syn conformation with a Mn–Mn distance of 4.72 Å. These carboxylate-bridged zigzag chains in **2** are further linked by (3-pyridyl)ethynylbenzoate ligands to four adjacent chains to form a 3-D coordination network having the same topology as **1**. The Mn–Mn separations between adjacent chains are 14.05 and 14.40 Å for the Mn atoms that are cis and trans to the coordinated 3-pyridyl nitrogen atom of the (3-pyridyl)ethynylbenzoate ligands, respectively. There is some $\pi-\pi$ interaction between the phenyl and pyridyl rings of the adjacent (3-pyridyl)ethynylbenzoate ligands with a centroid-to-centroid distance of

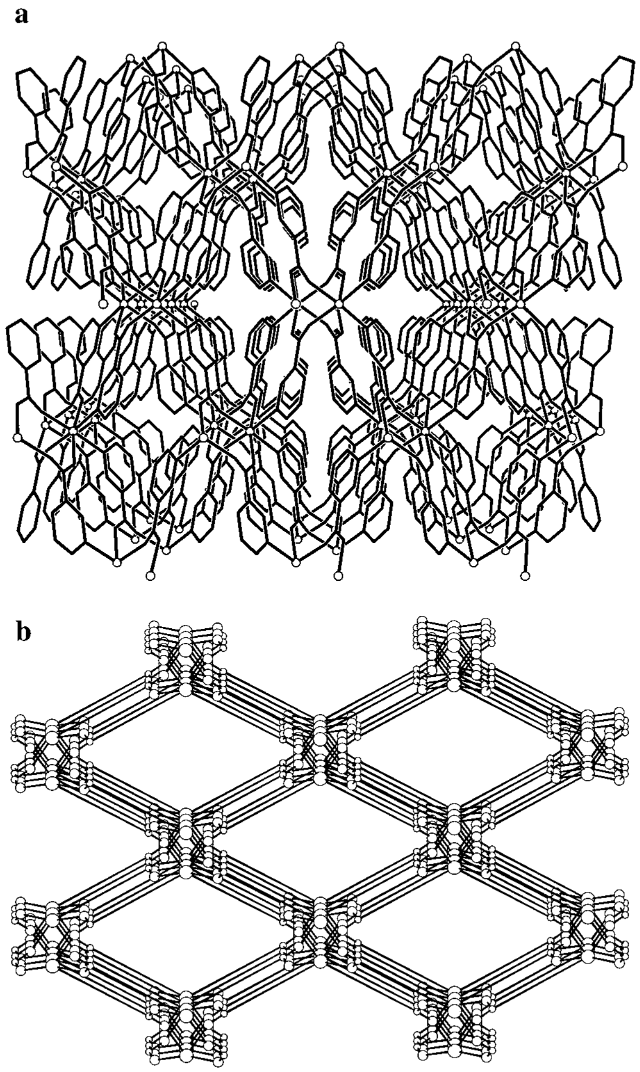


Figure 3. (a) Perspective view of the 3-D network in **1** down the *c* axis. Each doubly carboxylate bridged Mn−Mn chain (running along the *c* axis) is connected to four adjacent Mn−Mn chains to form a complicated 3-D network. (b) Connectivity of the 3-D network of **1** as viewed slightly off the *c* axis. Pyridyl groups are represented with straight lines. The doubly carboxylate bridged Mn−Mn chains orient along the *c* axis. The open circles with increasing sizes represent C, O, and Mn, respectively.

3.96 Å. We believe that the same bent configurations and rigid structures of the *m*-pyridinecarboxylate ligands in both **1** and **2** are responsible for their remarkably similar network topologies. The conjugate nature of (3-pyridyl)ethynylbenzoate ligands has forced the phenyl and pyridyl rings to be essentially coplanar with a dihedral angle of 9.6°.

X-ray structure determinations also indicate the absence of any solvate molecules in **1** and **2**, which has been further confirmed by thermogravimetric analyses (TGA). TGA curves for both **1** and **2** do not show any weight loss until the onset of decomposition at ∼360 °C.

Magnetic Results. Magnetic susceptibility data were collected on **1** and **2** in a 100 G applied field. X-ray structures of both **1** and **2** suggest that dominant magnetic interactions should occur along the carboxylate-bridged Mn(II)−Mn(II) chains. The magnetic data were satisfactorily fitted to numerical solutions to the one-dimensional Heisenberg Hamiltonian for $S = {}^{5}/_{2}$ as derived by Hiller et al.[23] based on the results of Weng.[24] Plots of χT vs T and fits to the 1-D Heisenberg antiferromagnetic chain model for **1** and **2** are shown in Figure 4. The expression used was

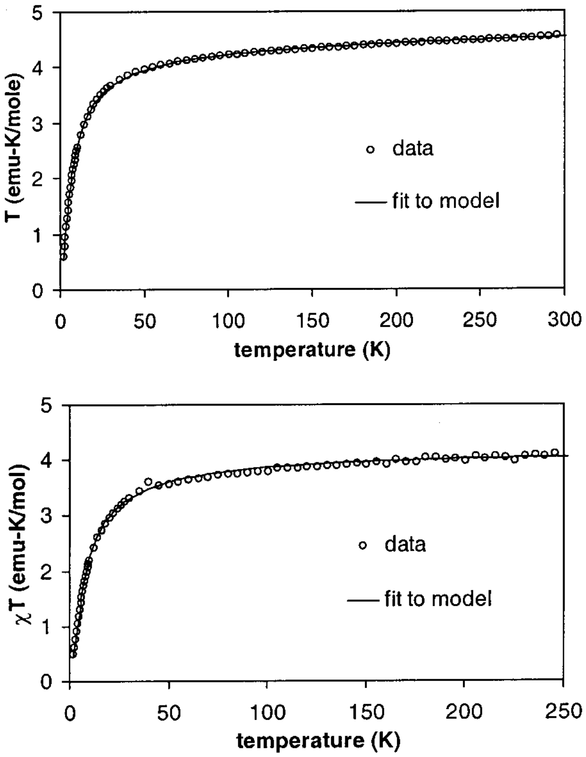


Figure 4. Plot of χT vs T measured at 100 G for (top) **1** and fit to eq 1 and (bottom) **2** and fit to eq 1.

$$\chi_M T = \frac{Ng^2\mu_B^2}{k} \frac{2.9167 + 208.04x^2}{1 + 15.543x + 2707.2x^3} \quad \text{where} \quad x = \frac{|J|}{kT} \qquad (1)$$

The two parameter nonlinear least-squares fits to the data yield $g = 2.03 \pm 0.05$ and $J/k = -0.47 \pm 0.05$ K for **1** and $g = 1.95 \pm 0.05$ and $J/k = -0.54 \pm 0.05$ K for **2**, respectively. These are in good agreement with $g = 2.00$ expected values for a ^{6}A Mn(II) ground state and weak coupling mediated by pairs of bridging carboxylate ligands. The fits can be improved slightly with the inclusion of a temperature-independent paramagnetism term, but the g and J values remain essentially the same.

On the basis of these results, both **1** and **2** thus appear to be new examples of one-dimensional Heisenberg antiferromagnetic chains. In comparison, the well-studied chain compounds $AMnCl_3{\cdot}2H_2O$, where A = Cs^+ or $[(CH_3)_4N]^+$, consist of face-sharing $MnCl_6$ octahedra and exhibit $J/k = -3.0$ and -6.3 K, respectively.[25,26] The couplings in **1** and **2** are, as expected, significantly weaker. However, the title compounds are free of the paramagnetic impurities that have complicated the analysis of the $AMnCl_3$-type materials.[27] The further examination of the magnetic properties of **1** and **2** at much lower temperatures would be interesting, for it should reveal a phase transition to a three-dimensionally ordered solid.

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In summary, we have synthesized two new 3-D Mn(II) coordination polymers based on *m*-pyridinecarboxylate ligands. X-ray structure determinations reveal that **1** and **2** exhibit very similar network topologies in spite of the different lengths of the nicotinate and (3-pyridyl)ethynylbenzoate groups, probably a result of the rigid, conjugate nature of the bridging ligands. Magnetic data indicate that both **1** and **2** are new examples of one-dimensional Heisenberg antiferromagnetic chains.

Acknowledgment. We acknowledge financial support from the National Science Foundation (CHE-9727900 and DMR-9875544 to W.L.; CHE-9727485 to G.T.Y.). We thank Dr. Scott R. Wilson and the Materials Chemistry Laboratory of University of Illinois for the collection of X-ray diffraction data and the National Institute of Standards and Technology for use of the SQUID magnetometer. W.L. is an Alfred P. Sloan Fellow, an Arnold and Mabel Beckman Young Investigator, and a Cottrell Scholar of Research Corporation.

Supporting Information Available: Four figures (depictions of X-ray structures and TGA curves of **1** and **2**) and an X-ray crystallographic file in CIF format for the structure determinations of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC000227V