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

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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.12,13 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 zr-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)ethylbenzoato]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 Perkin-Elmer 1000 FT-IR spectrometer. 1H and 13C 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 10 G applied field. Approximately 20 mg of I 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)ethylbenzoate. A mixture of 3-ethyl-4-pyridinecarboxylate (1.03 g, 10 mmol) and methyl 4-bromobenzoate (2.02 g, 10 mmol) in 50 mL of diethyl ether was refluxed in the presence of copper(I) iodide (10 mg, 0.05 mmol) for 20 h. Diethyl ether 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 MgSO4 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. 1H: δ 8.78 (br s, 1H, Hâ), 8.58 (br d, 1H, J = 4.8 Hz, Hb), 8.04 (d, 2H, J = 8.8 Hz, Hc), 7.83 (dt, 1H, J1 = 7.6 Hz, J2 = 2.0 Hz, Hf), 7.60 (d, 2H, J = 8.8 Hz, Hg), 7.31 (dd, 1H, J1 = 7.6 Hz, J2 = 4.8 Hz, Hj), 3.93 (s, 3H, CH3), 13C{1H} (δ): 166.4, 152.2, 148.9, 138.6, 131.6, 130.0, 129.6, 127.1, 123.1, 121.0, 91.8, 88.6, 52.3.

Synthesis of Bis(nicotinato)manganese(II), 1. A mixture of MnCl2·4H2O (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 MnCl2·H2NCOCH3: 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 (s), 1154 (m), 1034 (s), 1000 (m), 915 (s), 886 (m), 836 (m), 745 (m), 695 (m), 545 (w).

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nylbenzoate was synthesized in 67% yield by a Heck coupling for all non-hydrogen atoms. All of the hydrogen atoms in by full-matrix least squares using anisotropic displacement parameters.

Table 1. Data for the X-ray Diffraction of 1 and 2

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<td>499.37</td>
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* R1 = Σ|Fobs| − |Fcalc|/Σ|Fobs|; wR2 = [Σ[w(Fo − Fc)²]/Σ[w(Fo)²]₁/2; GOOF = [Σ[w(Fo − Fc)²]/(no. of reflections − no. of parameters)]₁/2.

Synthesis of Bis[4-(3-pyridyl)ethylbenzoato]manganese(II), 2. A mixture of Mn(ClO₄)₂·6H₂O (0.0904 g, 0.25 mmol) and methyl 4-(3-pyridyl)ethylbenzoate (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, the mixture was warmed to 110 °C. After 96 h of heating, the mixture was warmed to 110 °C. The shortest Mn separations between adjacent chains are 4.49 Å.

The ligand precursor methyl 4-(3-pyridyl)ethynylbenzonitrile under similar conditions.

Results and Discussion

Synthesis. The ligand precursor methyl 4-(3-pyridyl)ethylbenzoate was synthesized in 67% yield by a Heck coupling reaction between 3-ethylpyridine and methyl 4-bromobenzoate as illustrated in Scheme 1. Methyl 4-(3-pyridyl)ethylbenzoate was characterized by ¹H and ¹³C(¹H) NMR spectroscopy.

Bis(nicotinato)manganese, 1, was obtained as large pale yellow crystals in 88% yield by a hydro(solvo)thermal reaction between Mn(ClO₄)₂·6H₂O 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.

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)ethylbenzoato]manganese(II), 2, was obtained similarly by a hydro(solvo)thermal reaction between Mn(ClO₄)₂·6H₂O and methyl 4-(3-pyridyl)ethylbenzoate (Scheme 2). 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 C2/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) Å 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 groups 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 π−π 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 C2/c with one Mn atom and one (3-pyridyl)ethylbenzoate...
ligand in the asymmetric unit. As before, the Mn(II) 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.

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 π−π interaction between the phenyl and pyridyl rings of the adjacent (3-pyridyl)-ethynylbenzoate ligands with a centroid-to-centroid distance of

![Scheme 1](image)

![Scheme 2](image)

![Figure 1](image)

![Figure 2](image)
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 \( S = \frac{3}{2} \) as derived by Hiller et al.\(^{23}\) based on the results of Weng.\(^{24}\) Plots of \( \chi T \) 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

\[
\chi_M T = \frac{N g^2 \mu_B^2}{k} \left( \frac{2.9167 + 208.04 x^2}{1 + 15.543x + 2707.2x^3} \right)
\]

where \( x = \frac{|J|}{kT} \) (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 \( ^6A \) 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 AMnCl₃·2H₂O, where A = Cs⁺ or \([\text{CH}_3\text{N}]^+\), consist of face-sharing MnCl₆ 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 AMnCl₃-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.


In summary, we have synthesized two new 3-D \text{Mn(II)} coordination polymers based on \textit{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 \text{Heisenberg antiferromagnetic chains}.

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\textbf{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.

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