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One-pot Solvothermal Crystallization of Two Three-dimensional Manganese 2,6-Naphthalenedicarboxylates: Secondary Ligand-induced Pseudopolymorphism

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Two manganese 2,6-naphthalenedicarboxylates, [Mn(ndc)(DMF)] (**1**) and $[Mn_3(ndc)_3(DMF)_4]$ (**2**) (ndc: 2,6-naphthalenedicarboxylate), have been isolated from a one-pot reaction system. Single-crystal X-ray diffraction results indicate that both compounds exhibit three-dimensional porous structures. Compounds **1** and **2** can be considered pseudopolymorphs. Careful inspection of the structures of compounds **1** and **2** suggests that the spatial arrangement of a secondary ligand of DMF plays a crucial role in the formation of the two supramolecular isomers.

Porous coordination polymers (PCPs) or metal–organic frameworks (MOFs) have attracted extensive interest in the past two decades because of their potential applications as functional materials in gas storage,[1] separation processes,[2] drug delivery,[3] catalysis,[4] and chemical sensing,[5] coupled with their abundant structural diversity. This class of materials can be easily prepared through self-assembly of multidentate organic ligands as linkers and metal ions as connecting nodes. Through the wide choice of metals and infinite selection and design of ligands, a great number of PCPs have been obtained in this burgeoning field, and several are already available commercially. However, the deliberate design of such materials still presents considerable challenges. In particular, the final obtained structures can be influenced by many factors, including the coordination geometries of metal ions, spatial arrangements of ligands, synthetic approaches, solvent effects, and temptation by guests or counter ions. It has been shown that among the aforementioned factors, solvents often play crucial roles: they can serve as secondary ligands or guest molecules. As part of ongoing research work on PCPs of polycarboxylates, three porous cobalt(II) 1,3,5-benzenetricarboxylates have been successfully prepared in our group that are structurally dependent on the reaction solvent and additive.[6] Such interesting results have intrigued us to continue to explore the influence of solvent on the construction of PCPs. Among the most commonly used transition-metal elements in the realm of PCPs, manganese is attracting considerable interest because of its ability to function as progenitor of novel magnetic molecular materials. On the other hand, as a typical aromatic polycarboxylate ligand, 2,6-naphthalenedicarboxylic acid (2,6-H_2ndc) has been used as an excellent long linear rigid ligand for PCPs. For example, $[Zn_4O(ndc)_3]\cdot(DEF)_6$ was reported to have a large gas sorption capacity, while $[Mg_3(ndc)_3(DEF)_4]$ exhibited a high H_2 adsorption enthalpy.[7] Several manganese naphthalenedicarboxylate PCPs were also reported.[8] Herein, we present one-pot solvothermal crystallization of two three-dimensional (3-D) manganese 2,6-naphthalenedicarboxylates, [Mn(ndc)(DMF)] (**1**) and $[Mn_3(ndc)_3(DMF)_4]$ (**2**), and the spatial arrangement of the solvent as a secondary ligand on the final products and their structures.

Two kinds of crystals with distinct differences in morphology, needle for compound **1** while cubic for **2**, were synthesized from solvothermal reactions, one-pot of $MnCl_2\cdot4H_2O$ and 2,6-H_2ndc in DMF solution at 150 °C for three days.[9] While the bulk products are cocrystallized in one-pot, the yield of compound **1** (40%) is higher than that of **2** (10%) estimated on the basis of the morphology of crystals. Meanwhile, both compounds are air-stable and insoluble in water and most organic solvents. Compound **2** was previously synthesized by Xu and co-workers under solvothermal conditions with its structure reported.[10] We provide herein a brief discussion on the synthesis and characterization of compound **2** to illustrate the spatial arrangement of the secondary ligand with respect to the final products and their structures. TGA and XRD results of compound **1** are provided in Supporting Information.[14]

Single-crystal X-ray analysis reveals that **1** crystallizes in monoclinic space group $P2_1/c$ and features a 3-D porous structure.[11] There are one crystallographically independent Mn(II) center, two halves of ndc^{2-}, and one DMF molecule in the asymmetric unit. As shown in Figure 1, the Mn cation adopts six-coordination geometry with an average Mn–O distance of 2.1890 Å. Mn(1) is surrounded in a distorted octahedral fashion by five carboxylate oxygen atoms from four ndc^{2-} anions and one oxygen atom from a DMF molecule. The Mn cations are further bridged via pairs of carboxy groups to form a one-dimensional (1-D) rod, which can be considered an infinite rod-shaped secondary building unit (SBU).[12] Each rod is directly connected to four neighboring rods through the ndc ligands, resulting in the formation of a 3-D structure (Figure 2). 1-D channels are formed in compound **1** along the *c* axis, in which the DMF molecules protrude.

Compound **2** consists of linear trimeric Mn_3 cluster building units, which are linked through six carboxylate groups of the ndc ligands to form a 3-D framework. Compounds **1** and **2** can be considered pseudopolymorphs. Careful inspection of the structures of **1** and **2** suggests that the spatial arrangement of the secondary ligand of DMF plays a crucial role in the formation of these two pseudopolymorphs. Its different spatial arrangement forms two SBUs in the two compounds. As can be seen from Figure 3, in compound **1**, DMF serves as a secondary ligand residing on the equator sites of manganese octahedrons, thus

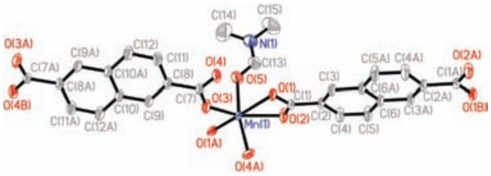

Figure 1. Coordination environment of Mn(II) cation in compound **1**. Hydrogen atoms are omitted for clarity.

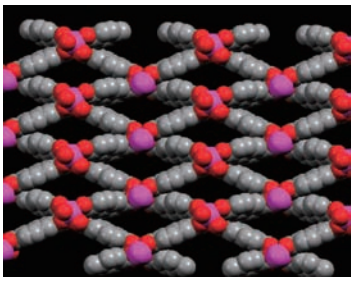

Figure 2. Crystalline framework of compound **1** drawn along the *c* axis, with coordinating DMF molecules omitted.

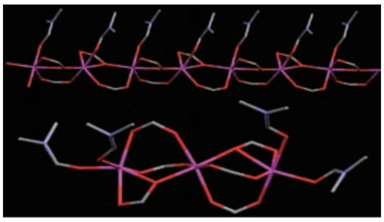

Figure 3. Rod-shaped secondary building unit in compound **1** (top) and trimeric metal building unit in compound **2** (bottom). Naphthalene rings are omitted for clarity.

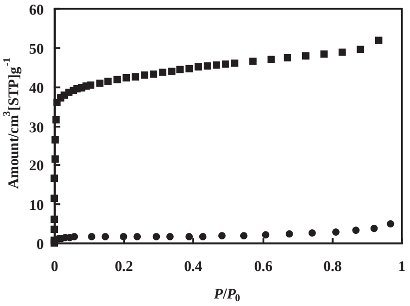

Figure 4. CO_2 (top) and N_2 (bottom) adsorption isotherms at 195 and 77 K for compound **1**, respectively. STP: standard temperature and pressure, P: CO_2 partile pressure, and P_0: saturated vapor pressure.

giving infinite Mn–O rod-shaped SBU, while in compound **2**, two DMF molecules occupy both the axis and equator sites of the two terminal Mn atoms in each Mn_3 cluster, forming linear trimeric Mn_3 SBU.

To study the porosity of desolvated **1**, carbon dioxide and nitrogen gas adsorption isotherms (Figure 4) were measured after DMF was removed under evacuation at 473 K. The Langmuir surface area calculated from the nitrogen gas adsorption data are $10\,m^2\,g^{-1}$, showing that only surface adsorption occurs. Such behavior has previously been described in PCPs with pore sizes of less than 10 Å.[13] The adsorption of CO_2 revealed a typical type I isotherm for microporous materials. The maximum amounts of desolvated **1** adsorbed is $49\,cm^3\,g^{-1}$ for CO_2 as measured at $P/P_0 = 0.9$. The Langmuir surface area calculated from CO_2 is $180\,m^2\,g^{-1}$. The quadrupole moment of CO_2 molecules presumably explains the remarkable uptake, since it can promote favorable interactions with the host, desolvated **1**.

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9 Compounds **1** and **2** were simultaneously synthesized under solvothermal conditions: a mixture of $MnCl_2 \cdot 4H_2O$ (0.198 g, 1.00 mmol), H_2ndc (0.218 g, 1.00 mmol), and DMF (10 mL) was stirred for 2 h, sealed in a Teflon-lined stainless steel autoclave (25 mL), kept at 150 °C for 3 days, and allowed to cool to room temperature. Colorless needle crystals of **1** and cubic crystals of **2** were obtained after the reaction mixture was filtered, washed with EtOH, and dried in air at ambient temperature. The crystals were separated by manual picking. Approximate yields: ca. 40% for **1** and 10% for **2** based on Mn. Anal. Calcd for **1** $C_{15}H_{13}MnNO_5$: C, 52.65; H, 3.83; N, 4.09%. Found: C, 52.27; H, 3.92; N, 3.98%. Anal. Calcd for **2** $C_{48}H_{46}Mn_3N_4O_{16}$: C, 52.44; H, 4.22; N, 5.09. Found: C, 52.05; H, 4.09; N, 5.01.

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11 Single-crystal X-ray data were collected at 293 K on a Rigaku Mercury diffractometer with Mo Kα radiation ($\lambda = 0.7107$ Å). The structure was solved with direct methods (SIR97), and refined with full-matrix least-squares on F^2. Crystal data for **1**. $C_{15}H_{13}NO_5Mn$ (293 K). fw 342.2, monoclinic, space group $P2_1/c$, $a = 9.652(2)$ Å, $b = 22.106(6)$ Å, $c = 7.5273(17)$ Å, $\beta = 110.759(5)°$, $V = 1501.8(6)$ Å^3, $Z = 4$, $D_{calcd} = 1.513\,g\,cm^{-3}$, absorption coefficient $0.901\,mm^{-1}$, total reflections collected 11384, unique 3385 ($R_{int} = 0.0364$), GOF = 1.069, $R1 = 0.0341$, $Rw = 0.0884$ ($I > 2\sigma(I)$). Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-830282. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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14 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.