



NOTE

Trinuclear Manganese Metal-Organic Frameworks Based on 2,6-Naphthalenedicarboxylic Acid

ZHIQIANG JIANG

Biology and Chemistry Engineering College of Panzhuhua University, Sichuan 617000, P.R. China

Corresponding author: E-mail: myjiangzq@163.com

(Received: 17 March 2012;

Accepted: 31 October 2012)

AJC-12354

A three-dimensional (3D) Mn(II) metal-organic frameworks $[\text{Mn}_{1.5}(\text{2,6-ntd})_{1.5}(\text{DMA})_2]$ (**1**; 2,6-ntd = 2,6-naphthalenedicarboxylic acid; DMA = *N,N'*-dimethylacetamide) based on trinuclear manganese subunit has been solvothermally prepared and structurally characterized by single-crystal X-ray diffraction. This compound crystallized in a monoclinic space group of C_2/c with $a = 14.3418(3) \text{ \AA}$, $b = 18.4597(3) \text{ \AA}$, $c = 20.9956(4) \text{ \AA}$, $\alpha = 90.00^\circ$, $\beta = 99.576(2)^\circ$, $\lambda = 90.00^\circ$, $V = 5481.03(18) \text{ \AA}^3$ and $Z = 4$.

Key Words: Trinuclear, Manganese, Metal-Organic Frameworks, 2,6-Naphthalenedicarboxylic acid.

The design and preparation of metal-organic frameworks have attracted much attention during the past decades owing to their structural diversities of the architectures, potential applications to gas separation and storage, catalysis, magnetism and fluorescence¹⁻¹⁰. The 2,6-naphthalenedicarboxylate (2,6-ntd) ligand is an adequate molecular building block for the construction of metal-organic frameworks. Because of its rigidity and stability one expects the resulting frameworks to be porous⁴⁻¹⁰. In the present study, we report a 3D open microporous metal-organic frameworks $[\text{Mn}_{1.5}(\text{2,6-ntd})_{1.5}(\text{DMA})_2]$ prepared by solvothermal methods.

The chemicals with reagent-grade quality were purchased from commercial sources and used without purification.

Preparation of compound: $[\text{Mn}_{1.5}(\text{2,6-ntd})_{1.5}(\text{DMA})_2]$ (**1**) was synthesized under solvothermal conditions using a 23 mL capped scintillation vial. In a typical reaction, $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.3217, 0.56 mmol), pyrazine (0.0306 g, 0.37 mmol), 1,2,4-triazole (0.0833 g, 1.21 mmol), 2,6-naphthalenedicarboxylic acid (0.1318 g, 0.61 mmol) were added to methanol (1.0 mL) and *N,N'*-dimethylacetamide (DMA, 4.0 mL). The reactants were stirred to form a clear solution prior to heating at 120 °C for 5 days. Yellow single crystals of $[\text{Mn}_{1.5}(\text{2,6-ntd})_{1.5}(\text{DMA})_2]$ suitable for X-ray diffraction were obtained.

X-crystallography: Suitable single crystals of $[\text{Mn}_{1.5}(\text{2,6-ntd})_{1.5}(\text{DMA})_2]$ were carefully selected under an optical microscope and glued to thin glass fibers. Whereafter, single-crystal X-ray diffraction analyses were performed on a computer-controlled XCalibur E CCD diffractometer with graphite-monochromated MoK_α radiation ($\lambda_{\text{MoK}_\alpha} = 0.71073 \text{ \AA}$)

at $T = 293.2 \text{ K}$. Empirical absorption corrections were made using the SADABS program¹¹. The structure was solved by direct methods and subsequent difference Fourier syntheses and refined using the SHELXTL software package¹². All non-hydrogen atoms were refined anisotropically and the hydrogen atoms on the ligand were placed in idealized positions and refined using a riding model.

Structure description: The X-ray crystal structure of **1** is shown in Fig. 1. In each independent crystallographic unit of **1**, the two metal centers adopt two different types of metal environments (Fig. 1a). Mn1 is bounded by six oxygen atoms from six bidentate carboxylate ends of 2,6-naphthalenedicarboxylic acid. Mn2 is six coordinated by four oxygen atoms from four bidentate carboxylate ends of 2,6-naphthalenedicarboxylic acid ligands, two oxygen atoms from two DMA molecules. Interestingly, as shown in Fig. 1b, complex **1** consists of linear trimeric Mn₃ clusters building block units, which are linked by four μ_2 -bridging carboxylate groups of the 2,6-naphthalenedicarboxylic acid ligands *via* bidentate coordination modes to form a two-dimensional (2D) layer (Fig. 1c). The 2D layers are further linked by carboxylate groups of the 2,6-naphthalenedicarboxylic acid ligands adopting tridentate coordination modes resulting in three-dimensional metal-organic framework (Fig. 1d). Although 3D frameworks have been constructed from 2,6-naphthalenedicarboxylic acid and other metal ions, they show structures different from that of **1**. The void space of the channels is filled with DMA molecules coordinating Mn(II) ions. The void volume may be generated after removal of the coordinating DMA molecules.

