

## NOTE

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

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A three-dimensional (3D) Mn(II) metal-organic frameworks  $[Mn_{1.5}(2,6-ntd)_{1.5}(DMA)_2]$  (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<sub>2</sub>/c with a = 14.3418(3) Å, b = 18.4597(3) Å, c = 20.9956(4) Å,  $\alpha = 90.00^\circ$ ,  $\beta = 99.576(2)^\circ$ ,  $\lambda = 90.00^\circ$ ,  $V = 5481.03(18) Å^3$  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 fluorescence<sup>1-10</sup>. The 2,6-naphthalenedicarboxylate (2,6ntd) 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 porous<sup>4-10</sup>. In the present study, we report a 3D open microporous metal-organic frameworks [Mn<sub>1.5</sub>(2,6-ntd)<sub>1.5</sub>(DMA)<sub>2</sub>] prepared by solvothermal methods.

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

**Preparation of compound:**  $[Mn_{1.5}(2,6-ntd)_{1.5}(DMA)_2]$  (1) was synthesized under solvothermal conditions using a 23 mL capped scintillation vial. In a typical reaction,  $Mn(NO_3)_2 \cdot 6H_2O$ (0.3217, 0.56 mmol), pyrazine (0.0306 g, 0.37 mmol), 1,2,4triazole (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*<sup>\*</sup>-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  $[Mn_{1.5}(2,6-ntd)_{1.5}(DMA)_2]$ suitable for X-ray diffraction were obtained.

**X-crystallography:** Suitable single crystals of  $[Mn_{1.5}(2,6-ntd)_{1.5}(DMA)_2]$  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<sub> $\alpha$ </sub> radiation ( $\lambda_{MoK\alpha}$ =0.71073 Å)

at T = 293.2 K. Empirical absorption corrections were made using the SADABS program<sup>11</sup>. The structure was solved by direct methods and subsequent difference Fourier syntheses and refined using the SHELXTL software package<sup>12</sup>. 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  $\mu_2$ -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 metalorganic 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.





Fig. 1. (a) Coordination environment of Mn in 1; (b) Trimeric Mn<sub>3</sub> building unit in 1; (c) The two-dimensional (2D) layer in 1; (d) View of the three-dimensional architecture of 1

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