

Microporous Manganese Formate: A Simple Metal–Organic Porous Material with High Framework Stability and Highly Selective Gas Sorption Properties

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Ordered porous materials such as zeolites are widely used in many practical applications including size- and shape-selective catalysis and separation by exploiting their well-defined channels and cavities.^{1,2} Design and synthesis of zeolite-like materials with specific structures and functions are thus important. However, rational design of such materials using the conventional solid state synthesis is extremely difficult. As a new approach to preparing porous materials, coordination of metal ions to organic linkers to build open frameworks has received much attention for the past decade because it allows more flexible and rational design of such materials.³ Though the framework instability such as the collapse of frameworks upon guest removal has been a serious shortcoming of these materials, the pioneering work of Yaghi and co-workers led to the successful synthesis of metal–organic frameworks with permanent porosity.⁴ Nevertheless, only a handful of metal–organic frameworks have been reported to possess permanent porosity in terms of reversible gas sorption behavior.^{3b,5} Studies on the functional aspects of metal–organic porous materials such as ion exchange,⁶ separation,⁷ gas storage,⁸ catalysis,⁹ sensor,^{7,10} and magnetism^{10,11} are slowly emerging. In particular, the remarkable ability of some of these materials in sorption of methane and hydrogen envisages their applications in the storage of these gases in the not-too-distant future. Furthermore, ordered porous materials capable of selective sorption of a certain gas would be useful in sensing and separating the gas, but few examples are known.^{5e,12} Herein we report the new metal–organic material: a microporous manganese formate that exhibits permanent porosity, high thermal stability, and highly selective gas sorption properties.

Heating a mixture of manganese(II) chloride and formic acid dissolved in diethylformamide (DEF)/1,4-dioxane in a sealed tube for 2 days produces porous manganese(II) formate as colorless polyhedral crystals, the composition of which is $\text{Mn}(\text{HCO}_2)_2 \cdot \frac{1}{3}(\text{C}_4\text{H}_8\text{O}_2)$ ($\mathbf{1} \cdot \frac{1}{3}\text{dioxane}$).¹³ The X-ray crystal structure of $\mathbf{1} \cdot \frac{1}{3}\text{dioxane}$ ¹⁴ (Figure 1) revealed a three-dimensional (3D), charge-neutral network composed of Mn(II) ions and formate anions in a 1:2 ratio. There are four crystallographically independent Mn(II) ions, each of which is coordinated by six formate anions in a distorted octahedral geometry while each formate anion is bound to three Mn(II) ions in a *syn-syn-anti* mode. The Mn–O distances are in the range of 2.12–2.23 Å, typical for high-spin Mn(II) complexes. The 3D network is built with corner- and edge-shared MnO_6 octahedra (Figure 1). Among the four independent Mn(II) centers, Mn(1) is connected to four neighboring Mn(1) centers via two Mn(2) and a Mn(3) and a Mn(4) linkage. The simplification of the 3D network in $\mathbf{1} \cdot \frac{1}{3}\text{dioxane}$ by connecting all the Mn(II) ions results in a distorted diamond net where the Mn(1) centers behave as tetrahedral four-connecting nodes, and each adamantane-

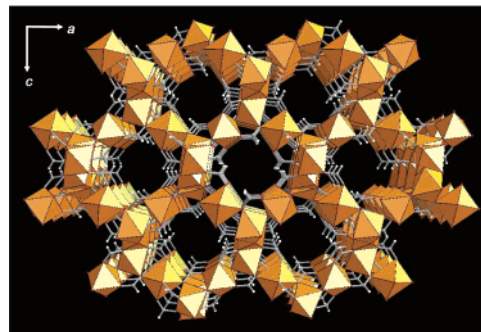


Figure 1. X-ray crystal structure of **1** showing channels along the *b* axis. Guest molecules are omitted. Each octahedron represents Mn(II) cation coordinated by six formate ligands.

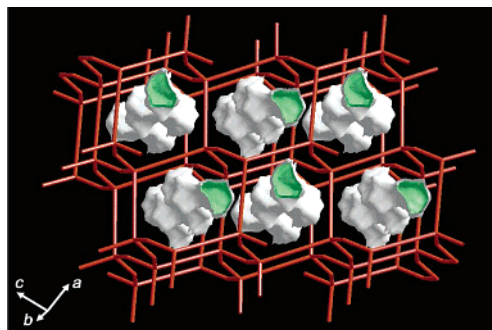


Figure 2. A simplified presentation of the network in **1**. Only Mn(II) centers are connected (red wire) to show the framework topology. Accessible zigzag open channels along the *b*-axis are shown as white surfaces with green entrances.

like cage is occupied by a guest molecule (see Supporting Information for a detailed description of the local connectivity and the framework topology). These cages with an internal diameter of 5.5 Å are connected to each other via a small window of approximately 4.5 Å to form a 1D zigzag channel along the *b* axis (Figure 2). The aperture is sufficient for the passage of small gas molecules. The accessible void volume of the channels lined by the formate ligands is estimated to be 33% of the total volume.¹⁵ The guest molecules occupying the channels can be removed at an elevated temperature without collapsing the host framework as confirmed by TGA, IR, and X-ray diffraction studies. The TGA data of $\mathbf{1} \cdot \frac{1}{3}\text{dioxane}$ reveal a weight loss (16.9%) in the range of 150–210 °C corresponding to the dioxane liberation from the compound, resulting in the guest-free manganese(II) formate microporous framework **1**, which starts decomposing at 350 °C. The framework is stable enough to maintain single-crystallinity after the complete guest removal at 150 °C under a reduced pressure. The structure of the framework determined by single-crystal X-ray

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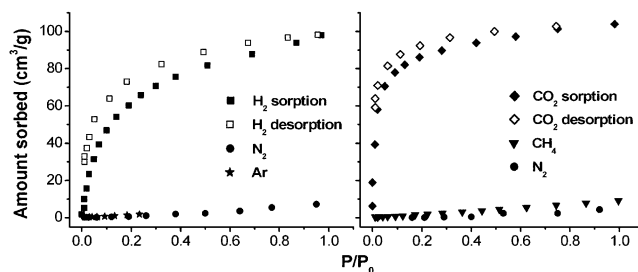


Figure 3. BET gas sorption isotherms at 78 K (left) and 195 K (right).

diffraction after the guest removal is essentially the same as before except for a small shrinkage of the unit cell parameters.¹⁶

To confirm the permanent porosity of **1**, gas sorption experiments were carried out. Despite the stable framework, to our surprise, no N₂ and Ar sorption was noticed at 78 K. Interestingly, however, slow but significant H₂ uptake was observed at the same temperature. The sorption of H₂ revealed a type I behavior typical for microporous materials (Figure 3) with a little hysteresis between sorption/desorption curves. The BET surface area of **1** is calculated to be ~240 m²/g, which is close to a typical value for microporous zeolites. However, the H₂ uptake of **1** at 78 K and 1 atm is notably higher (100 mL/g or 0.9 wt %) than that of the most favorable zeolite ZSM-5 (0.7 wt %). Because the H₂ sorption isotherm of **1** is not fully saturated, a higher hydrogen sorption capacity may be expected under higher pressures. Such selective sorption of H₂ in microporous solids is unprecedented. Furthermore, the selective sorption of CO₂ over N₂ or CH₄ by **1** at -78 °C is also observed (105 mL/g or 20 wt % uptake at 1 atm). The BET surface area of **1** calculated from the CO₂ sorption isotherm is 297 m²/g which is in good agreement with that from the H₂ sorption study at 78 K.

The selective sorption of H₂ and CO₂ may be attributed to the small aperture of the channels in **1**, which discriminates these gases with small kinetic diameters¹⁷ (2.8 and 3.3 Å, respectively) from other gases with larger kinetic diameters such as Ar, N₂, and CH₄ (3.4, 3.64, and 3.8 Å, respectively). These results suggest that **1** may behave as a highly effective size-selective molecular sieve which can discriminate, for example, between H₂ and N₂ or between CO₂ and CH₄; therefore, it may find important industrial applications such as the removal of CO₂ from natural gas as well as the recovery of H₂ from a mixture containing other gas molecules such as N₂, CO, and methane.¹⁸

Another implication of the gas sorption data is that the relative surface coverage¹⁹ of H₂ molecules in **1** at 78 K and 1 atm (150%) is much higher than those for other porous materials that have been reported to be promising for the H₂ storage by physisorption:²⁰ inorganic zeolites (22%), porous carbon materials (34%),²¹ and metal-organic framework MOF-5 (80%).^{8b} Further studies are needed to elucidate the mechanism of the H₂ sorption by **1**.

In conclusion, we synthesized a new metal-organic porous material, a microporous manganese formate with permanent porosity, high thermal stability, and highly selective gas sorption properties. It selectively adsorbs H₂ and CO₂ but not N₂ and other gases with larger kinetic diameters, which appears to be due to the small aperture of the channels. Despite a moderate H₂ storage capacity (yet higher than that of any zeolites), its H₂ surface coverage appears to be one of the highest among the known microporous materials. Thus this new zeolite-like material made of a simple organic building block may find useful applications in gas separation and sensor.

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Supporting Information Available: Description of experimental procedures, spectroscopic data, linear BET plots and X-ray crystallographic information as PDF and CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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