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Hysteretic Gas Sorption in a Microporous Metal–Organic Framework with Nonintersecting 3D Channels

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A permanently porous metal–organic framework (MOF) based on infinite chains of metal ions and angular dicarboxylate ligands was synthesized, and its unusual gas sorption properties were characterized. Zn^{2+} ions react with 2,7-ndcH_2 (2,7-naphthalenedicarboxylic acid) to produce a double-walled framework, [Zn(2,7-ndc)]. The porous MOF possesses narrow channels in three perpendicular directions. Gas sorption studies using Ar, CO_2, H_2, N_2, and O_2 at various temperatures reveal that saturation isotherms show a stepwise adsorption and hysteresis loops that are highly unusual features for microporous materials. The unexpected gas sorption behavior of the microporous MOF is due to the unique arrangement of the pore channels and their narrow passages comparable to the critical dimensions of adsorptive gases.
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Introduction

Studies on the gas sorption behavior of porous materials have been topical since a new type of openwork crystalline solids termed as metal-organic frameworks (MOFs) was reported to possess a permanent porosity.[1] The excellent gas sorption properties of these materials are of high interest not only for academic but also for practical reasons.[2] For example, such issues as the sequestration of CO_2 or harmful gases or the efficient storage of hydrogen require immediate attention from researchers in both science and industry.[3] One of the key questions underlying these applications is how gas molecules interact with solid surfaces of different chemical and physical nature. Therefore, understanding the physisorption of gases in MOFs with various pore environments is important.

Theories developed decades ago provide satisfactory explanations for the physisorption of gases in most porous materials including MOFs.[4] Some of the theories, however, are based on relatively simple assumptions[5] and probably on limited knowledge about the detailed structures of sorbents. MOFs, unlike other types of porous solids, allow structural characterizations at an atomic resolution owing to their high crystallinity. Therefore, irregularities observed in the gas sorption studies of MOFs, if any, can be correlated with the geometrical features of the pores, and in turn, this knowledge would significantly improve our chances to develop novel materials for practical applications.

In our systematic approach towards new MOFs based on angular dicarboxylate ligands, and their gas sorption properties,[6] we discovered that a microporous MOF with a well-defined framework shows unexpected gas sorption behavior. The crystal structure and basic characterizations are reported here.

Results and Discussion

Solvothermal reactions of $Zn(NO_3)_2\cdot 6H_2O$ and 2,7-naphthalenedicarboxylic acid (2,7-ndcH_2) under carefully adjusted conditions yield small polyhedral crystals as a singular phase. The crystals are found to be a new MOF with the composition [Zn(2,7-ndc)] (**1**) according to X-ray crystallographic analysis. The homogeneity and purity of the bulk product were verified by elemental analysis and X-ray powder diffraction (XRPD) measurements (see below).

The structure of **1** is based on zig–zag-type 1D arrays of Zn^{2+} ions that are bridged by carboxylate groups of 2,7-ndc (Figure 1a). The metal ions in the infinite chain have alternating tetrahedral and octahedral environments. A single chain is connected to four neighbors through 2,7-naphthalene backbones. Therefore, the overall net appears to be a double-walled square grid framework, and straight open channels are visible when **1** is viewed along the *c* axis (Figure 1b).

MOFs based on this type of 1D building blocks [or rod-shaped SBUs (secondary building units)] are known, and they have been well studied.[7] However, **1** is unique from those predecessors in that the solvent channels are open to three perpendicular directions. Note that separated 1D channels result when infinite chains are interlinked by linear dicarboxylate ligands.

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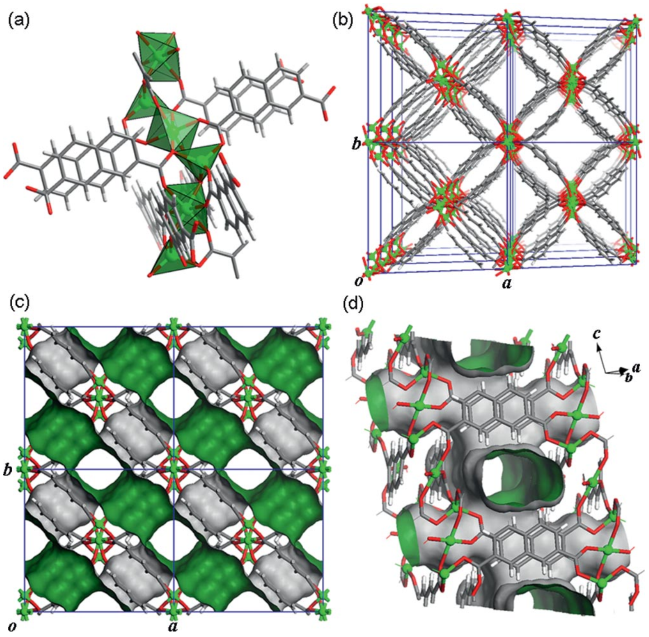

Figure 1. (a) Part of the infinite 1D chain of Zn^{2+} ions; (b) Perspective view of the net; (c) Cross-sectional view [(001)] of the Connolly surface of **1**; (d) detailed view showing the arrangement of the channels along the three directions.

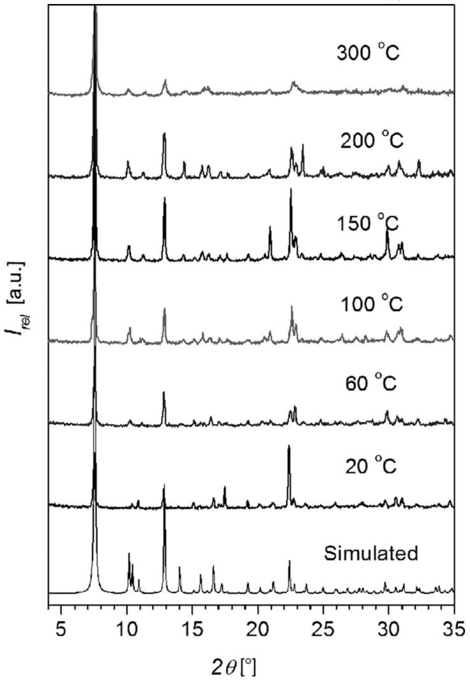

Figure 2. Temperature-dependent X-ray powder diffraction patterns of **1** measured upon heating from room temperature. The sample was held at designated temperatures for at least 30 min.

In contrast to the simple structure of the framework, the pore structure of **1** deserves some elaboration. The solvent-accessible voids, 40% of the total crystal volume,[8] are characterized by three channels that are in mutually perpendicular directions (Figure 1c). Of those, two channels are along the two diagonals of the *ab* plane, and they are related by *c*-glide plane symmetry. This implies that the size and shape of the two channels are identical and that they do not intersect. The free passages of these channels are 5–6.5 Å. The third channel runs along the *c* direction and passes through the two channels on the *ab* plane (Figure 1d). This channel is somewhat narrower with the free passage of 4–5.5 Å, which is measured from the Connolly surface of 1.4 Å probe radius.[9] As we will show below, the unique pore structure and the narrow free passages of **1** would not allow efficient diffusion of guest molecules in the pores.

The thermal stability of **1** was unambiguously established by XRPD measured upon heating from room temperature (Figure 2). A number of strong peaks are observed even at 200 °C in the positions expected from the single-crystal structure. A prolonged heating at 300 °C leads to a gradual degradation in the diffraction patterns. Therefore, the open framework of **1** is estimated to be stable to about 200–300 °C in air.

The accessibility of the void space of **1** was verified by gas sorption studies. As expected, numerous gases such as Ar, CO_2, H_2, N_2, and O_2 were found to adsorb and desorb. The results are shown in Figure 3, and the analysis from saturation isotherms is summarized in Table 1.

What is unexpected, however, is the results that the saturated sorptions of Ar, CO_2, N_2, and O_2 at 87, 195, 77, and

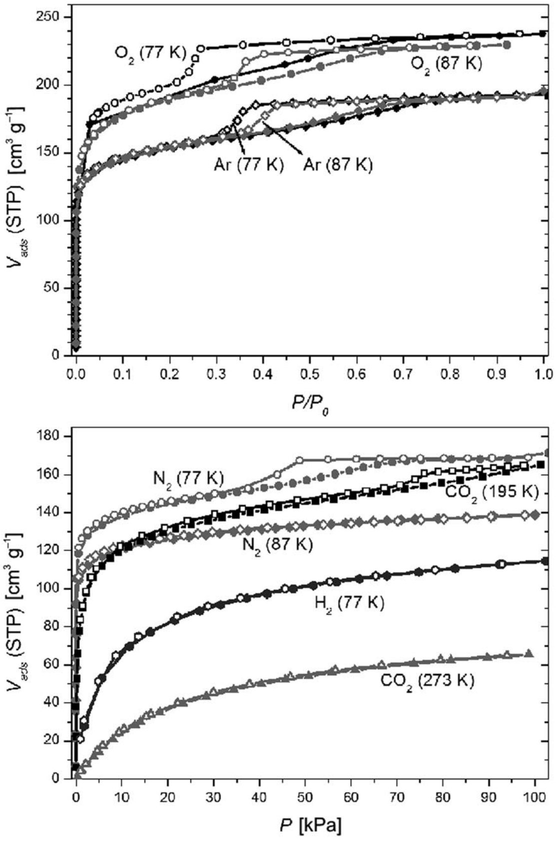

Figure 3. Gas sorption isotherms of O_2, Ar, N_2, and CO_2 for **1** measured at designated temperatures. Filled and open symbols denote adsorption and desorption, respectively.

Table 1. Summary of gas sorption analysis for [Zn(2,7-ndc)].

Adsorptive (T [K])	A_{BET} [m^2 g^{-1}]	$A_{langmuir}$ [m^2 g^{-1}]	V_{pore} [cm^3 g^{-1}]	Porosity [%][a]	Critical dimensions [Å][b]
O_2 (87)	657	769	0.284	36	2.93/2.99
N_2 (77)	520	686	0.265	34	2.99/3.05
CO_2 (195)	636	840	0.207	26	3.19/3.34
Ar (87)	501	636	0.246	31	3.40

[a] V_{pore} [cm^3 g^{-1}] × $\rho_{crystal}$ [g cm^{-3}] × 100. [b] Ref.[12]; the value for Ar is the kinetic diameter.

87 K, respectively, show stepwise adsorptions with marked hysteresis loops. Among the four adsorptives, CO_2 displays the least pronounced hysteresis at relative pressures much higher than others. The onset of adsorption steps is independent of gases or temperature, but hysteresis loops are slightly enlarged at lower temperatures judging from the sorptions of Ar and O_2 at 77 K. The hysteresis is observed only when the isotherms approach the saturated vapor pressure of adsorptives ($P/P_0 = 1$), and thus no hysteresis is observed in the sorption of H_2, N_2, and CO_2 at 77, 87, and 273 K, respectively, up to 1 bar.

The hysteretic adsorption/desorption profiles of **1** resemble the type IV isotherm or type H2 hysteresis according to IUPAC classifications.[10] The former is related to pore condensations in mesoporous materials, and the latter is associated with disordered materials that have ill-defined distributions of pore size and shape.[11] With the unambiguous crystal structure and the robust nature of the framework, these possibilities are ruled out in the case of **1**. A dynamic deformation of the framework upon desolvation is unlikely either judging from the XRPD shown in Figure 2.

Instead, we propose that the nonintersecting arrangement of the channels and narrow passages are responsible for the hysteresis. The narrow and indented channels with a nonintersecting structure result in "bottle-neck" effects and inefficient diffusion of adsorptive gases in **1**. Therefore, the void spaces between bottle-necked regions will be occupied very slowly and incompletely. Under this situation, the desorption of the adsorbates in the hindered pores would occur at pressures lower than they were adsorbed, similar to the case of capillary condensations in mesoporous materials leading to a hysteresis. The fact that porosities measured from the saturated sorptions of Ar, CO_2, N_2, and O_2 are all lower than the expected value of 40% (Table 1) suggests the presence of kinetically hindered regions.

It has been argued that the diffusion and exclusion of adsorptive gases in porous solids with pores of fixed size depends on critical molecular dimensions rather than more commonly used kinetic diameters.[12] This is because the orientations of adsorptive molecules are ignored in kinetic diameters.[13] On the basis of the critical dimensions of O_2, N_2, CO_2, and Ar (Table 1), the former two gases are expected to adsorb in **1** more readily than the other two. Indeed, the total pore volumes of **1** determined by using the four gases are much higher for O_2 and N_2 than for Ar and CO_2.[14] Therefore, this work is a rare example demonstrating that the orientations of adsorptive molecules play an important role when pores are sufficiently narrow. A MOF with pores any smaller than those of **1** should display selective sorption behavior.

Conclusions

The combination of infinite 1D chains and angular dicarboxylate linkers leads to a noninterpenetrating MOF, [Zn(2,7-ndc)], with 3D channels. This can be compared to earlier studies[7] where infinite chains and linear dicarboxylates give isolated 1D channels. [Zn(2,7-ndc)] is a typical microporous material with a well-defined framework and pore structures; however, unusual hysteresis following stepwise adsorptions is observed, a feature characteristic for mesoporous materials. The unexpected behavior is attributed to a kinetic hurdle imposed by the nonintersecting channels with free passages approaching the critical dimensions of adsorptive gases. This work emphasizes the importance of structural analysis in understanding the physisorption of gases in MOFs.

Experimental Section

General: All the reagents and solvents were commercially available and used as received. The X-ray powder diffraction patterns were recorded with a Bruker D8 Advance system equipped with a Cu sealed tube (λ = 1.54178 Å). BET gas sorption isotherms were measured with a Belsorp Mini-II (BEL Japan, Inc). Details of the measurements are available in the Supporting Information.

Synthesis of [Zn(2,7-ndc)] (1): To a solution of $Zn(NO_3)_2 \cdot 6H_2O$ (0.119 g, 0.40 mmol) and 2,7-ndcH_2 (0.087 g, 0.40 mmol) dissolved in DMF (2.6 mL) was added NEt_3 (0.222 mL, 0.40 mmol), and the solution was vigorously stirred for 2 h. The clear solution was sealed in a glass vial, and then heated to 110 °C for 20 h. Polyhedral crystals thus obtained were guest-exchanged with CH_3CN and $CHCl_3$ and evacuated by heating to 150 °C for 12 h under vacuum (0.015 g, 13%). $C_{12}H_6O_4Zn$ (279.56): calcd. C 51.55, H 2.16; found C 51.51, H 2.85.

Crystallography: Single crystals were directly picked up from the mother liquor, attached to a glass fiber, and transferred to a cold stream of liquid nitrogen (–70 °C) for data collections. The full hemisphere data were collected with a Siemens SMART CCD diffractometer with Mo-K_α radiation (λ = 0.71073 Å). After the data integration (SAINT) and semiempirical adsorption correction based on equivalent reflections (SADABS), the structure was solved by direct methods and subsequent difference Fourier techniques (SHEXLTL). All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added to their calculated positions. The extra-framework solvent molecules are severely disordered, and the diffused electron densities could not be modeled properly. Therefore the data were treated with the SQUEEZE routine of PLATON, and the results were attached to the CIF file. After final refinements, relatively large difference peak (1.5 e Å^{-3}) and hole (–1.8 e Å^{-3}) were found; however, they are at senseless places (<0.4 Å from Zn1 and Zn2) and therefore ignored. The crystal data and results of structure refinements are summarized in Table S1. CCDC-740777 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Details of the gas sorption measurements; TGA plot; FTIR spectra of **1** before and after activation.

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[14] Note that the total pore volume is the more honest reporter of sorption capacities than specific surface areas because the latter is based on somewhat over-simplified assumptions.

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