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Metal–Organic Framework Based on a Trinickel Secondary Building Unit Exhibiting Gas-Sorption Hysteresis

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An interpenetrating microporous metal–organic framework based on a μ_3-oxotrinickel basic carboxylate secondary building unit has been synthesized and structurally characterized. It exhibits pronounced gas-sorption hysteresis and selective adsorption of carbon dioxide over methane.

Porous metal−organic frameworks (MOFs)[1] have attracted widespread interest in the past decade because of their fascinating structures[2] and intriguing potential applications. Studies in catalysis,[3] magnetism,[4] nonlinear optics,[5] separation,[6] and gas storage[7] illustrate the versatility of MOFs and their application potential. Their amenability to design,[8] exceptionally high surface area,[9] and framework flexibility[1b,10] set porous MOFs apart from traditional zeolites[11] and carbonaceous materials.[12] Introduction of weak interactions such as hydrogen bonding and $\pi-\pi$ interaction into the architecture of porous materials can not only improve the framework flexibility but also induce interpenetration in MOFs.[1b,13] Although interpenetration is generally considered to reduce the porosity,[14] it can tune the pore size in MOFs for their application in gas separation.[15] For the above reasons, MOFs based on weak interactions may be particularly useful for selective gas adsorption. Herein, we report an interpenetrating microporous nickel MOF, PCN-5 (PCN represents a porous coordination network), exhibiting gas-adsorption selectivity of carbon dioxide over methane and pronounced gas-sorption hysteresis.

A solvothermal reaction between $Ni(NO_3)_2{\cdot}6H_2O$ and H_3TATB (TATB represents 4,4′,4″-*s*-triazine-2,4,6-triyltribenzoate) in dimethylformamide (DMF) using a Teflon-lined autoclave afforded light-green crystals of PCN-5 (yield 50%) with an overall formula of $H_2[Ni_3O(H_2O)_3(TATB)_2]{\cdot}5DMF{\cdot}2H_2O$, which was determined by X-ray crystal-

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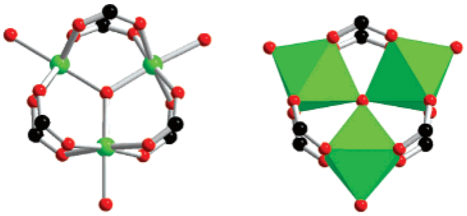
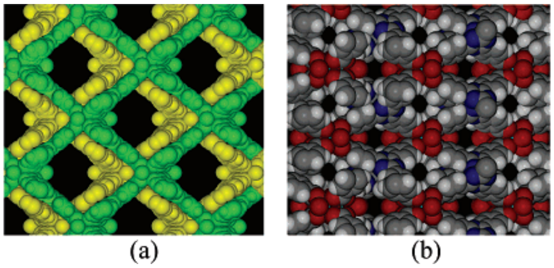


Figure 1. μ_3-Oxotrinickel basic carboxylate SBU (carbon, black; oxygen, red; nickel, green).

lography, elemental analysis, and thermogravimetric analysis (TGA).

Single-crystal X-ray crystallographic studies[16] revealed that PCN-5 crystallizes in monoclinic space group $C2/m$. PCN-5 adopts a trimeric μ_3-oxo-centered basic carboxylate cluster $[Ni_3O(O_2CR)_6(H_2O)_3]^{2-}$ (Figure 1) as its secondary building unit (SBU) with an average Ni$-\mu_3$-O distance of 2.019 Å. In a SBU, the three Ni atoms and the μ_3-O atom are on the same plane. Each pair of Ni centers are bridged by two carboxylate groups from two different TATB ligands, and the coordination geometry of each Ni center is octahedral when the terminal aqua ligand is considered (average Ni$-$O distance 2.126 Å). These trigonal-planar basic carboxylate clusters, $[M_3O(O_2CR)_6(L)_3]$, where M represents trivalent metal ions (Al^{3+}, Cr^{3+}, Fe^{3+}),[17] have been previously employed as SBUs for the construction of MOFs. Trigonal-planar basic carboxylate clusters with divalent metal ions, however, are rare in both small molecules and MOFs.[18]

Each trinickel SBU connects six TATB ligands, and each TATB ligand binds three trinickel SBUs to form a binodal (3,6)-connected net. Similar to that found in other TATB MOFs,[19] $\pi-\pi$ interaction between TATB ligand pairs has also been observed in PCN-5. In previously reported TATB MOFs, the triazine rings of each TATB pair are in the staggered conformation, leading to strong $\pi-\pi$ interaction.[19] In PCN-5, however, the central triazine rings of each TATB pair are in a dislocated conformation (Figure S1 in the Supporting Information). The distance between the centers of the two triazine rings is 4.471 Å, but the distance between the two ligands is 3.385 Å, indicating $\pi-\pi$ interactions. Overall, PCN-5 possesses a 2-fold interpenetrated structure (Figure 2a).



(a) (b)

Figure 2. (a) 2-fold interpenetrating network of PCN-5, viewed from the [0 0 1] direction. (b) Space-filling model from the [1 0 0] direction showing hydrophobic (white) and hydrophilic (red) channels.

In the [1 0 0] direction, there exist two types of open channels (Figure 2b): One is hydrophilic, with two trinickel SBUs opposite to each other and a SBU$-$SBU distance of 4.928 Å (terminal O$-$terminal O). The other is hydrophobic, surrounded by four TATB ligands, with a channel size of 5.334 × 4.977 Å (C$-$C). In the [0 1 0] direction, the trinickel SBUs are connected by TATB ligands to form hydrophilic channels with the distance between the terminal aqua ligands of opposite SBUs 4.928 Å (O$-$O) (Figure S2 in the Supporting Information), while in the [0 0 1] direction, large channels containing opposite trinickel SBUs can be found (Figure 2a). The shortest distance between two opposite terminal aqua ligands is 11.413 Å (O$-$O).

TGA (Figure S4 in the Supporting Information) indicates that the first weight loss of 23.1% from 50 to 200 °C corresponds to the loss of five DMF guest molecules (calcd 24.0%), which is closely followed by the loss of two water solvates and three aqua ligands (found 6.1%; calcd 6.0%) on the SBU up to 300 °C. Decomposition of the TATB ligands starts at 300 °C and ends at 560 °C with an overall weight loss of 57.2% (calcd 57.5%), leaving a black residue of NiO (found 13.6%; calcd 12.5) behind.

The permanent porosity of PCN-5 is verified by gas-sorption isotherms (Figure 3) and powder X-ray diffraction (PXRD) studies (Figure S3 in the Supporting Information).

A freshly prepared sample of PCN-5 was soaked in methanol for 3 days to remove DMF guest molecules. Subsequently, the sample was soaked in dichloromethane for 3 days more to remove methanol solvates and then pumped under a dynamic vacuum at 25 °C overnight to activate the sample.

Based on the TGA results and the activation temperature, it can be inferred that the aqua ligands on the SBUs should remain in the activated sample and the protonated water solvates should stay connected to these terminal aqua ligands through hydrogen bonding. Crystallographic studies showed electron density for the water solvates, but a clear picture of the hydrogen-bonding network could not be established because the solvates are highly disordered. An attempt to remove the aqua ligands and water solvates by heating other samples at 100 °C or higher under a dynamic vacuum resulted in the collapse of the framework.

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(16) X-ray crystal data for PCN-5: $C_{48}H_{30}N_6O_{16}Ni_3$, $M_r = 1122.91$, monoclinic, $C2/m$, $a = 30.175(3)$ Å, $b = 21.108(3)$ Å, $c = 16.762(2)$ Å, $\alpha = 90.00°$, $\beta = 123.188(2)°$, $\gamma = 90.00°$, $V = 8934.7(18)$ Å^3, $Z = 4$, $T = 293$ K, $\rho_{calcd} = 0.835$ g/cm^3, R1 $[I > 2\sigma(I)] = 0.0476$, wR2 $= 0.1304$, GOF $= 0.949$.

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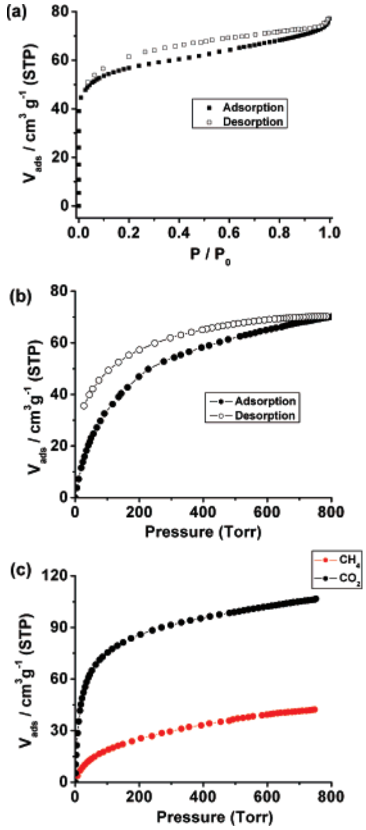

Figure 3. (a) Nitrogen sorption isotherm at 77 K. (b) Hydrogen adsorption−desorption isotherms at 77 K. (c) Carbon dioxide and methane adsorption isotherms at 195 K.

The nitrogen sorption isotherm (Figure 3a) of an activated sample reveals a Langmuir surface area of 225 m^2/g and a pore volume of 0.13 cm^3/g. As shown in Figure 3a, the nitrogen adsorption hysteresis can be attributed to the dynamic feature of the framework that arises from the hydrogen-bonding network formed by terminal aqua ligands and water solvates in the large hydrophilic channel.[1b,10a,20] This assessment is also consistent with the observed selective adsorption behavior of PCN-5 (vide infra).

The hydrogen adsorption isotherm (Figure 3b) indicates an uptake of 70 cm^3/g (0.63 wt %) for PCN-5 at 77 K and 760 Torr. Because the hydrogen adsorption isotherm is not saturated, a higher hydrogen uptake is expected under higher pressures. The hydrogen adsorption data follow the Langmuir−Freundlich equation[21] closely and predict a saturation of 0.8 wt % for PCN-5 at 77 K. These values are lower than those of other reported MOFs[7c,19b−d,20,22] but comparable with those of zeolites, ZSM-5 (0.7 wt %),[6d] and higher than those of mesoporous silica materials (MCM-41, 0.5 wt %).[23] As shown in Figure 3b, the sorption isotherm also displays noticeable hysteresis because of the framework flexibility arising from the hydrogen-bonding network. The kinetic effect in narrow pores may also be a contributing factor to the hysteresis because the adsorption/desorption kinetics were very slow.[24] Similar behavior has only been observed recently.[25] The hysteretic hydrogen sorption thus may offer the possibility of developing new porous MOFs, which can upload hydrogen at high pressures and store it at low pressures.[25]

To check the selective adsorption properties of PCN-5, carbon dioxide and methane adsorption studies were carried out at 195 K. As shown in Figure 3c, the carbon dioxide uptake by PCN-5 at 195 K and 760 Torr can reach 210 mg/g (4.8 mmol/g), while the methane uptake under the same conditions is limited to 30 mg/g (1.9 mmol/g). The selective adsorption of carbon dioxide (kinetic diameter 3.3 Å) over methane (3.8 Å) can be attributed to the molecular-sieving effect. When van der Waals radii of the channel wall are considered, a channel with an atom−atom distance of 4.98 Å corresponds to an opening of about 3.3 Å. The 11.413 Å channels shown in Figure 2a should be largely blocked by the hydrogen-bonding network (vide supra). The boiling point difference between the two gases may also contribute to the adsorption selectivity. A similar molecular-sieving effect has also been observed recently in manganese formate,[6d] chromium terephthalate,[6f] a cobalt MOF,[6g] and a nickel MOF.[6h]

In conclusion, an interpenetrating microporous nickel MOF (PCN-5) constructed from a μ_3-oxotrinickel basic carboxylate SBU has been synthesized and structurally characterized. Gas-sorption studies indicate that PCN-5 exhibits both hysteretic hydrogen sorption and exciting gas-adsorption selectivity. Future work will focus on developing MOFs with high gas-adsorption selectivity and high hydrogen uptake.

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Supporting Information Available: Structure figures, TGA plots, PXRD data, and complete crystallographic data (CIF) for PCN-5. This material is available free of charge via the Internet at http://pubs.acs.org.

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