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A Metal−Organic Framework with Entatic Metal Centers Exhibiting High Gas Adsorption Affinity

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The lack of an effective, economic, and safe on-board vehicular gas (hydrogen or methane) storage method is one of the major technical barriers preventing fuel-cell driven automobiles to compete with traditional ones.[1] Recently, the gas-storage properties of metal−organic frameworks (MOFs) have been actively explored.[2] In the area of hydrogen storage, suggested strategies to increase hydrogen uptake include using pore sizes comparable to gas molecules[3] and introducing coordinatively unsaturated metal centers.[4] Both strategies boil down to the enhancement of gas affinity of the material. Recent inelastic neutron scattering studies suggest that high-affinity H_2 binding sites are metal-based.[5] These recent findings prompted us to search for new ways to increase the gas affinity of metal centers in MOFs.

In metalloproteins, such as hemoglobin, reversible O_2 binding is achieved by utilizing an iron active center (Figure 1a), where a porphyrin ligand and a histidine residue force the iron center into a square pyramidal geometry, generating an open coordination site for gas binding. Similarly, in Vitamin B_{12} (VB_{12}), the central cobalt is surrounded by a corrin and a proximal ligand, and the distal position is open for substrate binding.[6] Herein we report a MOF with a novel secondary building unit (SBU, Figure 1b), containing four hemoglobin/VB_{12}-like cobalt centers bundled through sharing a μ_4-oxo bridge, producing four metal centers at an entatic state (vide infra) for gas binding. This MOF exhibits exceptional gas adsorption affinity for a number of gases.

In bioinorganic chemistry, an entatic state is a state in which an unusual geometry is *imposed* by the protein polypeptides on a metal center whose reactivity in electron transfer, substrate binding, or catalysis is enhanced.[7] Similarly, due to the specific geometric requirements of the ligands and SBUs in a MOF, the metal centers can be forced into an entatic state to enhance their affinity toward gases.

Entatic metal centers (EMCs) represent a biomimetic approach to coordinatively unsaturated metal centers (UMCs).[8] The latter are frequently obtained by removal of one or more ligands from a metal center to achieve coordinative unsaturation; the ligand removal required to achieve UMCs may collapse the entire network.[9] Conversely, most of the EMCs are ready for substrate binding without the need for ligand removal.

Herein we report a MOF with EMCs, $H_2[Co_4O(TATB)_{8/3}]$, designated PCN-9 (Porous Coordination Network) for convenience. TATB (4,4′,4″-*s*-triazine-2,4,6-triyltribenzoate) is a ligand developed in this laboratory for its planar conformation, potential ability to bind additional metal atoms, and high thermal stability of resulting MOFs.[4b,10] PCN-9 crystals were grown under solvothermal conditions by a reaction between H_3TATB and cobalt nitrate in DMSO at 135 °C.

X-ray single-crystal analysis[11] revealed that PCN-9 crystallizes in the $Im\bar{3}m$ space group. It adopts a square-planar $Co_4(\mu_4\text{-}O)$ SBU, with a μ_4-oxo residing at the center of a square of four Co atoms. All four Co atoms in the SBU are five-coordinate with square-pyramidal geometry. The Co−μ_4-O distance is 2.351(2) Å. If one of the five-coordinate Co atoms is compared to the active center in hemoglobin, the μ_4-O is analogous to the proximal ligand, and on the opposite side of the square-pyramidal base is the distal position of the Co, which is below the plane of the four O atoms in an entatic state, and ready to bind a substrate to achieve octahedral coordination. Although a tetrahedral μ_4-oxo bridge is common,[12] a square-planar μ_4-oxo bridge is rare. Only a few examples have been found in iron,[13a] copper,[13b] vanadium,[13c] and niobium[13d] compounds. The square-planar μ_4-oxo bridge found in PCN-9 is unique in a MOF. Every $Co_4(\mu_4\text{-}O)$ SBU connects eight trigonal-planar TATB ligands, and every TATB ligand connects three $Co_4(\mu_4\text{-}O)$ SBUs to form a (8,3)-net. Alternatively, this (8,3)-net can also be described as a three-dimensional network formed by corner sharing of octahedral cages (Figure 2a); the O_h-cage is defined by six $Co_4(\mu_4\text{-}O)$ SBUs at the corners and eight TATB ligands on the faces. Overall, the structure of PCN-9 can be obtained by the interpenetration of two (8,3)-nets, the second being generated through translation along [1 1 0].

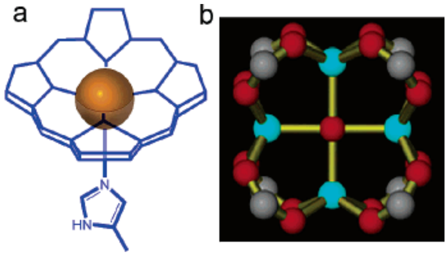

Figure 1. (a) Schematic drawing of the active center of hemoglobin. The gold sphere represents an Fe atom. (b) The $Co_4(\mu_4\text{-}O)(\text{carboxylate})_4$ SBU found in PCN-9. Color scheme: C, gray; Co, aqua; and O, red.

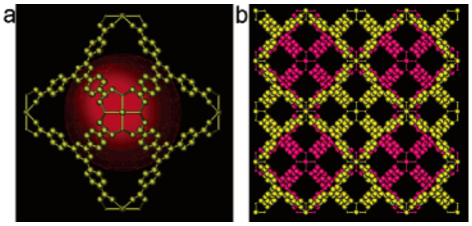

Figure 2. (a) Crystal structure of PCN-9 showing an octahedral cage; the red sphere represents void inside the cage. (b) View of the crystal structure of PCN-9 along the *a*-axis; the two interpenetrated networks are shown in gold and pink, respectively. All atoms are shown in arbitrary scales.

The volume of the octahedral cage is 2740 Å^3. Each open window of the cage is 6.7 × 6.7 Å (atom to atom distance) and possesses two EMCs with distal sites pointing toward the void. The solvent accessible volume of PCN-9 calculated using PLATON[14] is 58.8%. The permanent porosity of PCN-9 is confirmed by its N_2 adsorption isotherm. After desolvation, PCN-9 exhibits a Langmuir surface area of 1355 m^2/g and a pore volume of 0.51 cm^3/g.

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To determine the gas affinity of PCN-9, adsorption isotherms were collected at various temperatures, and the data were fit using the Langmuir−Freundlich equation.[15] Isosteric adsorption enthalpies as a function of the quantity of gas adsorbed were calculated using a variant of the Clausius−Clapeyron equation.[16,18a,b]

At low coverage, PCN-9 exhibits an O_2 adsorption enthalpy of 17.8 kJ/mol, comparable to that of Co exchanged zeolites (15.1−18.5 kJ/mol).[17] Similarly, at low coverage, the CO adsorption enthalpy of PCN-9 reaches 21.0 kJ/mol. These results represent the first measurement of O_2 or CO adsorption enthalpy in MOFs.

H_2 adsorption isotherm at 77 K indicates that PCN-9 has an uptake of 1.53 wt % at 760 Torr. Hydrogen adsorption isotherms at two other temperatures were collected and used to calculate the heat of adsorption. At low coverage, the heat of adsorption of PCN-9 for H_2 is 10.1 kJ/mol, which is higher than that of MOF-5 (5.2 kJ/mol), Prussian blue (7.4 kJ/mol), MOF-74 (8.3 kJ/mol), or HKUST-1 (6.6 kJ/mol) and is comparable to that of IRMOF-11 (9.1 kJ/mol) or a magnesium MOF (9.5 kJ/mol).[18]

In VB_{12}, the active center can bind a methyl or an alkyl group.[6] It is expected that PCN-9, with its SBUs structurally similar to the active center of VB_{12}, should have a high methane affinity. The CH_4 isotherms of PCN-9 at three temperatures were collected, corresponding to an adsorption enthalpy of 23.3 kJ/mol at low coverage. To the best of our knowledge, this is by far the highest CH_4 adsorption enthalpy found among MOFs (IRMOF-6 = 12.1 kJ/mol, MIL-53 = 17 kJ/mol).[19]

To further confirm that this remarkable enhancement of gas affinity is due to the EMCs, freshly prepared PCN-9 crystals (or a guest-free sample) were soaked in a dilute tetrabutylammonium cyanide solution in THF (1 mg/mL) for 2 days until the color of the crystals changed from violet to dark red. An IR spectra using this dark-red polycrystalline sample showed a sharp peak at 2105 cm^{-1}, a $+50$ cm^{-1} shift of the $C\equiv N$ stretch relative to that of free cyanide, consistent with the literature value for terminal cyanides bound to Co atoms.[20]

Aware that the bulkiness of the counterion may prevent cyanide ions from permeating into the channels, we decided to use CO as an IR probe. A guest-free PCN-9 sample was kept under a CO atmosphere (3 bar) overnight. IR spectra of the sample showed a peak at 2044 cm^{-1} (compared to 2143 cm^{-1} for free CO),[21] indicating terminal CO binding to the EMCs. The same sample was then kept under dynamic vacuum for 0.5 h to remove CO guests. The 2044 cm^{-1} feature disappeared, demonstrating the reversibility of EMC binding, consistent with CO adsorption measurements.

In summary, EMCs have been created based on the geometric requirements of a MOF. This approach is analogous to the formation of protein EMCs, which are enforced by surrounding polypeptides. The EMC-containing MOF possesses exceptionally high affinity to a number of commercially relevant gases. In particular, the H_2 and CH_4 adsorption enthalpies of PCN-9 are among the highest reported thus far. The biomimetic strategy presented here will be generally applicable in the search of new adsorptive materials to meet the requirements of on-board vehicular gas storage.

Additionally, the EMCs inside the open channels of PCN-9 make them ideal candidates for size- and/or shape-selective catalysis. This line of research is currently underway in our laboratory.

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Supporting Information Available: Detailed experimental procedures, X-ray structural data, thermogravimetric analysis, and gas adsorption data. This material is available free of charge via the Internet at http://pubs.acs.org.

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