Selective gas adsorption in a microporous metal–organic framework constructed of Co^{Π}_4 clusters[†]

Young Eun Cheon and Myunghyun Paik Suh*

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A porous metal–organic framework, $[Co^{II}_4(\mu-OH_2)_4(MTB)_2$: (H₂O)₄]_n·13nDMF·11nH₂O (SNU-15), has been prepared; the X-ray crystal structure reveals a CaF₂-like structure that generates 3D channels and the desolvated solid $[Co^{II}_4 (\mu-OH_2)_4(MTB)_2]_n$ (SNU-15') exhibits selective gas sorption properties for H₂ and O₂ gases over N₂ at 77 K, with exceptionally high O₂ density, as well as for CO₂ over CH₄ at 195 and 273 K, suggesting its potential application in gas separation processes.

Porous metal–organic frameworks (MOFs) have attracted great attention because of their potential applications in gas storage^{1–5} and separation processes,^{6,7} ion exchange,⁸ catalysis,⁹ sensor technology,¹⁰ and fabrication of metal nanoparticles.¹¹ In particular, porous materials that selectively absorb O₂ over N₂ are very important because they have potential to be applied in the separation of these gases from air: pure O₂ gas is utilized in combustion systems, medical treatment, and chemical processing, while high-purity N₂ is used for purging, blanketing and providing an atmosphere for metal treatments and other purposes. The selective adsorption of H₂ over N₂ is also important because of its potential application for the H₂ enrichment from N₂/H₂ exhaust in ammonia synthesis. Despite their importance, MOFs that show selective gas adsorption behaviour are not so common.^{6,7}

Here we report a 3D porous MOF, $[Co^{II}_{4}(\mu-OH_{2})_{4}-(MTB)_{2}(H_{2}O)_{4}]_{n}\cdot 13nDMF\cdot 11nH_{2}O$ (SNU-15). The MOF shows a fluorite-like structure that is quite rare in MOFs, ¹²⁻¹⁴ although it is frequently encountered in minerals. The desolvated solid of SNU-15 adsorbs O₂ and H₂ gases selectively over N₂, with extraordinarily high O₂ density.

The solvothermal reaction of $Co(NO_3)_2 \cdot 6H_2O$ and methanetetrabenzoic acid (H₄MTB) in DMF/EtOH/H₂O (3 : 1 : 1 v/v, DMF = *N*,*N'*-dimethylformamide) at 90 °C yielded **SNU-15**. The X-ray crystal structure of **SNU-15** reveals that the 3D framework is constructed from a linear Co^{II}_4 cluster as the rectangular secondary building unit and MTB⁴⁻ as the tetrahedral organic building block, and imitates the fluorite (CaF₂) structure.[‡]

In SNU-15, there exist two crystallographically independent cobalt atoms, Co1 and Co2, both of which have octahedral coordination geometry (Fig. 1a). They are connected in the sequence of Co1-Co2-Co2-Co1 by the carboxylate oxygen atoms of MTB⁴⁻ and aqua bridges to form a linear Co^{II}₄ cluster unit. The distances of Co1-Co2 and Co2-Co2 within a cluster unit are 3.550(1) Å and 3.428(1) Å, respectively. The Co1 and Co2 ions are linked by two carboxylates and an aqua bridge (O5), and the two Co2 ions are connected by two aqua bridges (O8). There have been a few reports of aqua bridged Co^{II} complexes.¹⁵ The carboxylate groups of MTB⁴⁻ bind metal ions in two different coordination modes; a monodentate mode in binding Co1 ions and a bidentate mode in bridging Co1 and Co2 ions. The central carbon atom of the MTB⁴⁻ ligand shows a tetrahedral geometry with an average bond angle of 111.8(1)°.

In SNU-15, each Co_4 cluster is linked with eight different MTB⁴⁻ ligands, as an eight-connecting rectangular parallelepiped secondary building unit (SBU), and each MTB⁴⁻ links four different Co_4 clusters, as a four connecting tetrahedral organic building block, which gives rise to the fluorite (CaF₂) structure where Ca^{2+} is eight coordinate and F⁻ is in tetrahedral environment (Fig. 2). It has been reported that the solvothermal reactions of H₄MTB with Cd²⁺ and Zn²⁺ resulted in the CaF₂¹³ and PtS¹⁶ structures, respectively. SNU-15 generates 3D channels extending parallel to the crystallographic *a*, *b*, and *c* axes. On the *ac* and *bc* planes, channels with rhombic apertures are created, which are alternately arranged perpendicularly to each other (see ESI†).



Fig. 1 (a) An ORTEP drawing of **SNU-15** with atomic numbering scheme (thermal ellipsoids with 30% probability). Symmetry operations: a, -x + 2, -y + 1, *z*; b, *x*, *y*, -z; c, -x + 2, -y + 1, -z. Network structure of **SNU-15** seen on the *ab* plane (b), on the *ac* plane (c), on the *bc* plane (d). Color scheme: Co^{II}, blue; oxygen, red; carbon, gray.

Department of Chemistry, Seoul National University, Seoul 151-747, Republic of Korea. E-mail: mpsuh@snu.ac.kr; Fax: +82-2-886-8516; Tel: +82-2-880-7760

[†] Electronic supplementary information (ESI) available: Experimental details, schematic view showing the arrangement of channels, and surface views of SNU-15, PXRD patterns, TGA/DSC trace, H₂ sorption isotherms at 77 K and 87 K, a plot of isosteric heat vs. degree of H₂ adsorption, O₂ sorption isotherms at 77 K and 290 K, XPS data, a plot of μ_{eff} vs. T, and tables of crystallographic data and magnetic susceptibility data. CCDC 714762. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b900085b



Fig. 2 A view of **SNU-15**, showing the CaF₂-like network structure constructed of a rectangular parallelepiped Co^{II}_{4} cluster and a tetrahedral MTB⁴⁻ organic building block. Color scheme: cobalt, green; oxygen, red; carbon, gray.

The effective aperture sizes of the channels extending along the a, b, and c axes, respectively, are $6.0 \times 8.0 \text{ Å}^2$, $5.8 \times 6.3 \text{ Å}^2$, and $13.8 \times 11.5 \text{ Å}^2$ (Fig. 1 and ESI†). Since the guest molecules could not be defined by the X-ray diffraction data measured even at 153 K due to the high thermal disorder, they were characterized by the elemental analysis data and IR spectra as well as TGA data. The free void volume estimated by PLATON¹⁷ is 67.6% and 69.5% of the total volume, respectively, with and without coordinated terminal aqua ligands.

Thermogravimetric analysis (see ESI[†]) indicates weight losses of 11.0% at 65 °C and 37.5% at 330 °C, which correspond to the loss of 15 water (calcd 10.8%) and 13 DMF (calcd 37.8%) molecules. The solid is thermally stable up to 400 °C. The powder X-ray diffraction (PXRD) pattern of SNU-15 is coincident with the simulated pattern derived from the X-ray single crystal data of SNU-15 (see ESI[†]), implying that the bulk sample is same as the single crystal.

When SNU-15 was heated at 220 °C under vacuum for 24 h, $[Co^{II}_4(\mu-OH_2)_4(MTB)_2]_n$ (SNU-15') resulted, in which every metal ion contains a vacant coordination site by liberating the terminal aqua ligand as well as guest solvent molecules as evidenced by elemental analysis and TGA data (see ESI†). SNU-15' lost transparency accompanying the color change from pink to violet, and we failed to determine its single crystal X-ray structure. The PXRD pattern of SNU-15' shows very broad peaks, and the original structure of SNU-15 was not restored even when SNU-15' was exposed to the vapor of DMF/H₂O (10 : 0.2, v/v) at 38 °C for 120 h (see ESI†). It can be assumed that the pore opening of SNU-15' is much smaller than SNU-15, and does not permit DMF or H₂O molecules to enter the channels.

To check the porosity of **SNU-15**', gas sorption was measured for N₂, H₂, O₂, CH₄, and CO₂ gases (Fig. 3). The samples for gas sorption experiments were prepared by heating **SNU-15** at 220 °C under vacuum for 24 h to remove all guest solvent molecules as well as coordinated aqua ligands. Despite the broadened PXRD pattern, **SNU-15**' adsorbs these gases to show Type I isotherms, characteristic of the microporous material. Some MOFs having broad PXRD patterns also adsorb gases to show permanent porosity.^{7c,18} **SNU-15**' adsorbs a significant amount of H₂ (82.1 cm³ g⁻¹ at STP) and O₂ (114 cm³ g⁻¹ at STP) but a very limited amount of N₂ (21.6 cm³ g⁻¹ at STP) at 77 K. The selective sorption must be mainly associated with the smaller kinetic diameters of H₂, CO₂, and O₂ than those of N₂ and CH₄ (H₂, 2.8;



Fig. 3 Gas sorption isotherms for **SNU-15**'. (a) N_2 (\blacksquare), H_2 (\blacktriangle), and O_2 (\bullet) at 77 K. (b) CO_2 (\blacksquare) and CH_4 (\blacktriangle) at 195 K (black) and 273 K (blue), respectively. Filled shape, adsorption; open shape, desorption.

CO₂, 3.3; O₂, 3.46; N₂, 3.64; CH₄, 3.8 Å).¹⁹ In addition, the significant quadrupole moment of CO₂ (-1.4×10^{-39} C m²) might induce a stronger interaction with the host framework than for CH₄.²⁰

SNU-15' adsorbs CO₂ gas up to 15.3 wt% (3.48 mmol g⁻¹, 78.02 cm³ g⁻¹ at STP) at 195 K and 1 atm, and 7.02 wt% (1.59 mmol g⁻¹, 35.7 cm³ g⁻¹ at STP) at 273 K and 1 atm. The highest CO₂ gas uptake at 273 K and 1 atm reported so far is 38.5 wt% for SNU-5.³ The multipoint DR (Dubinin–Radushkevich) surface area of SNU-15', which is estimated from the CO₂ sorption data in the range $P/P_0 = 0.004-0.09$, is 356 m² g⁻¹. The DR pore volume is 0.165 cm³ g⁻¹, which is far below the crystallographic pore volume of SNU-15' (1.03 cm³ g⁻¹). This suggests that SNU-15' is significantly collapsed or shrunk by the removal of the guests and the coordinated aqua ligands.

SNU-15' adsorbs 0.74 wt% of H₂ gas (4.70 H₂ molecules per formula unit) at 77 K and 1 atm, which is higher than Mirkin's amorphous infinite coordination polymers (0.57 wt%)¹⁸ but much lower than the values (2.5–2.9 wt%) for the best MOFs such as MIL-101,²¹ HKUST,²² SNU-5,³ and SNU-6.⁴ However, the isosteric heat of H₂ adsorption is 15.1 kJ mol⁻¹ (see ESI†), which is significantly higher than those (4.8–12.9 kJ mol⁻¹) of other MOFs.^{1a,3,23,24} The exceptionally high isosteric heat of H₂ adsorption in **SNU-15**' must be attributed to the vacant coordination site on every Co^{II} ion. It has been revealed that the vacant coordination sites in the MOF increase the interaction energy between H₂ molecules and the host framework.^{1a,3,24}

SNU-15' adsorbs O₂ gas up to 16.5 wt% at 77 K and 0.19 atm, (114 cm³ g⁻¹ at STP, 6.57 O₂ molecules per formula unit). The O₂ isotherm was measured only up to 147 Torr (0.193 atm) since the saturation vapor pressure of O₂ is 147.8 Torr at 77 K. The highest O₂ uptake capacity at 77 K and 0.19 atm reported so far is 618 cm³ g⁻¹ (950 kg m⁻³) in Co(BDP).²⁵ Interestingly, the O₂ adsorption isotherm exhibits three steps with marked hysteresis on desorption (see ESI†). In an initial step, **SNU-15**' adsorbs 10.4 wt% O₂ (4.18 mol mol⁻¹, 72.5 cm³ g⁻¹ at STP) at 77 K and 0.00077 atm, and in the second step it uptakes 14.3 wt% O₂ (5.75 mol mol⁻¹, 99.9 cm³ g⁻¹ at STP) at 77 K and 0.013 atm. After reaching a point at 0.013 atm, the O₂ adsorption still increases and the total amount of adsorbed O₂ becomes 16.5 wt% (6.57 mol mol⁻¹,

114 cm³ g⁻¹ at STP) at 0.20 atm. The fact that SNU-15' adsorbs 4 O₂ molecules per formula unit in the initial step indicates that an O₂ molecule is bound at every vacant coordination site of Co^{II} ion in the initial step, and the rest (2.57 molecules per formula unit) of the adsorbed O₂ molecules occupy the free space of SNU-15'. Similar stepwise gas adsorption behavior has been reported for other MOFs and explained by guest-induced structural transitions on gas adsorption or multiple MOF-adsorbate interactions that differ in energy.^{26,27} The O₂ adsorption density in SNU-15', as estimated by applying the pore volume measured by the CO_2 isotherm, is 998 kg m⁻³ at 0.19 atm. It is the highest among those of the MOFs reported so far, and the value suggests that O₂ gas is highly compressed within the pores, given that the density of liquid O_2 is 1140 kg m⁻³. SNU-15' also adsorbs O_2 up to 6.36 cm³ g⁻¹ (0.37 mol mol⁻¹) at 290 K and 1 atm.

In conclusion, we have prepared a new metal–organic framework that imitates the fluorite structure. It exhibits selective gas sorption properties for H_2 and O_2 gases over N_2 , and for CO_2 over CH_4 . In particular, the present material adsorbs O_2 with extraordinarily high density. The material has potential applications in the separation of O_2 and N_2 from air and also in H_2 enrichment from N_2/H_2 exhaust mixtures resulting from ammonia synthesis.²⁸

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Notes and references

‡ Crystal data for SNU-15: C₃₈H₄₈Co₄O₂₄, Mr = 1364.00, orthorhombic, space group Pnnm, a = 15.5094(4), b = 17.8251(5), c = 24.2210(7) Å, V = 6696.1(3) Å³, Z = 2, T = 298(2) K, $d_{\text{calc}} = 0.677$ g cm⁻³, $F_{000} = 1392$, Mo_{Kα} radiation, $\lambda = 0.71073$ Å, $\theta_{\text{max}} = 13.75$, 14830 reflections collected, 7872 unique ($R_{\text{int}} = 0.0728$). Final GOF = 0.846, $R_1 = 0.0601$, w $R_2 = 0.1716$, R indices based on 7872 reflections with $I > 2\sigma(I)$ (refinement on F^2), 203 parameters, 0 restraints. CCDC 714762.

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