Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Temperature-Triggered Gate Opening for Gas Adsorption in Microporous Manganese Formate

Hyunuk Kim[1], Denis G. Samsonenko[1], Minyoung Yoon[1], Ji Woong Yoon[2], Young Kyu Hwang[2], Jong-San Chang[2,*], and Kimoon Kim[1,*]

[1]National Creative Research Initiative Center for Smart Supramolecules, and Department of Chemistry, Pohang University of Science and Technology, Pohang 790-784, Republic of Korea, and [2]Catalysis Center for Molecular Engineering Korea Research Institute of Chemical Technology PO Box 107, Yusung, Daejeon 305-600, Republic of Korea
E-mail: kkim@postech.ac.kr or jschang@krict.re.kr

General Methods. All the reagents and solvents were purchased from commercial sources and used without further purification. Solvothermal reactions were carried out in sealed glass tubes. The single-crystal X-ray diffraction data of $M(HCOO)_2$ (M = Mn and Mg) were collected on a ADSC Quantum 210 CCD diffractometer with synchrotron radiation at Pohang Accelerator Laboratory. Gas sorption isotherms were recorded volumetrically with the Autosorb 1MP instrument in the temperature range of 77–196 K and in the pressure range of 10^{-5}–1.0 atm. Highly pure gases were used for the measurements.

Synthesis. $M(HCOO)_2$ (M = Mn and Mg): $Mn(HCOO)_2 \cdot \frac{1}{3}THF$ (**1**·⅓THF) and $Mg(HCOO)_2 \cdot \frac{1}{3}$dioxane (**2**·⅓dioxane) were synthesized according to our procedure published previously.[1,2] **1**·⅓THF was evacuated at 150 °C for 2 days under dynamic vacuum and **2**·⅓dioxane at 200 °C for 10 days under dynamic vacuum to remove the guests. Complete removal of guests in **1** and **2** has also been confirmed by elemental analysis and ^{1}H-NMR spectroscopy. Anal. Calcd for $C_2H_2O_4Mn_2$ (**1**): C, 16.57 H, 1.39. Found: C, 16.53; H, 1.49. Anal. Calcd for $C_2H_2O_4Mg_2$ (**2**): C, 21.01 H, 1.76. Found: C, 20.70; H, 1.91. ^{1}H-NMR spectra taken after digesting the activated crystals in DCl/D_2O showed no signals for the guest molecules.
$Co(HCOO)_2 \cdot \frac{1}{3}$DMF: A solution of $Co(ClO_4)_2 \cdot 6H_2O$ (0.732 g, 2.0 mmol) and HCOOH (184 mg, 4.0 mmol) in DMF solution (12 mL) was heated at 110°C in a sealed glass tube. After 48 h pink crystals were collected to give $Co(HCOO)_2 \cdot \frac{1}{3}$DMF (0.25 g, 72 %). $Ni(HCOO)_2 \cdot \frac{1}{3}$DMF: A solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.732 g, 2.0 mmol) and HCOOH (184 mg, 4.0 mmol) in DMF solution (12 mL) was heated at 100 °C in a sealed glass tube. After 48 h green powders were collected to give $Ni(HCOO)_2 \cdot \frac{1}{3}$DMF (0.132 g, 38 %). Guest-free samples for gas sorption measurements were prepared by heating $M(HCOO)_2 \cdot \frac{1}{3}$DMF (M = Co and Ni) at 130 °C for 2 days under dynamic vacuum.

X-ray crystallography. X-ray diffraction data of **1** and **2** were collected at 90K and 196K with a ADSC Quantum 210 CCD diffractometer using synchrotron radiation (λ = 0.73000 Å) at the Macromolecular Crystallography Wiggler Beamline 4A, Pohang Accelerator Laboratory (PAL), Pohang, Korea. Data reduction and adsorption correction were performed with HKL2000 package. The structures were solved by direct methods, and the refinements were carried out with full-matrix least-squares on F^2 with SHELXTL package. Crystal data for **1** (90 K): $C_2H_2O_4Mn$, M = 144.98, monoclinic, $P2_1/n$ (No. 14), a = 11.719(1) Å, b = 10.172(1) Å, c = 14.920(1) Å, β = 91.553(1)°, V = 1777.9 (3) Å^3, Z = 12, T = 90 K, $\mu(\lambda$ = 0.73000 Å) = 2.292 mm^{-1}, ρ_{calc} = 1.625 g·cm^{-3}, $2\theta_{max}$ = 50.0°, 5171

reflections measured, 2720 unique (R_{int} = 0.0824), R_1 = 0.0497 (2578 reflections with $I > 2\sigma(I)$), wR_2 = 0.1337 (all data), GOF = 1.084, 194 parameters and no restraints, CCDC 693551. Crystal data for **1** (196 K): $C_2H_2O_4Mn$, M = 144.98, monoclinic, $P2_1/n$ (No. 14), a = 11.732(1) Å, b = 10.200(1) Å, c = 14.947(1) Å, β = 91.538(1)°, V = 1788.0 (3) Å^3, Z = 12, T = 196 K, $\mu(\lambda$ = 0.73000 Å) = 2.279 mm^{-1}, ρ_{calc} = 1.616 g·cm^{-3}, $2\theta_{max}$ = 50.0°, 5103 reflections measured, 2724 unique (R_{int} = 0.1309), R_1 = 0.0765 (2532 reflections with $I > 2\sigma(I)$), wR_2 = 0.2005 (all data), GOF = 1.059, 194 parameters and no restraints, CCDC 693550. Crystal data for **2** (90 K): $C_2H_2O_4Mg$, M = 114.35, monoclinic, $P2_1/n$ (No. 14), a = 11.341(1) Å, b = 9.849(1) Å, c = 14.547(1) Å, β = 91.388(1)°, V = 1624.4(2) Å^3, Z = 12, T = 90 K, $\mu(\lambda$ = 0.73000 Å) = 0.250 mm^{-1}, ρ_{calc} = 1.403 g·cm^{-3}, $2\theta_{max}$ = 50.0°, 4820 reflections measured, 2568 unique (R_{int} = 0.0330), R_1 = 0.0294 (2470 reflections with $I > 2\sigma(I)$), wR_2 = 0.0914 (all data), GOF = 1.085, 194 parameters and no restraints, CCDC 693549. Crystal data for **2** (196 K): $C_2H_2O_4Mg$, M = 114.35, monoclinic, $P2_1/n$ (No. 14), a = 11.359(1) Å, b = 9.885(1) Å, c = 14.584(1) Å, β = 91.370(1)°, V = 1637.1 (2) Å^3, Z = 12, T = 196 K, $\mu(\lambda$ = 0.73000 Å) = 0.248 mm^{-1}, ρ_{calc} = 1.392 g·cm^{-3}, $2\theta_{max}$ = 52.0°, 5357 reflections measured, 2878 unique (R_{int} = 0.0321), R_1 = 0.0283 (2694 reflections with $I > 2\sigma(I)$), wR_2 = 0.0877 (all data), GOF = 1.063, 194 parameters and no restraints, CCDC 693548.

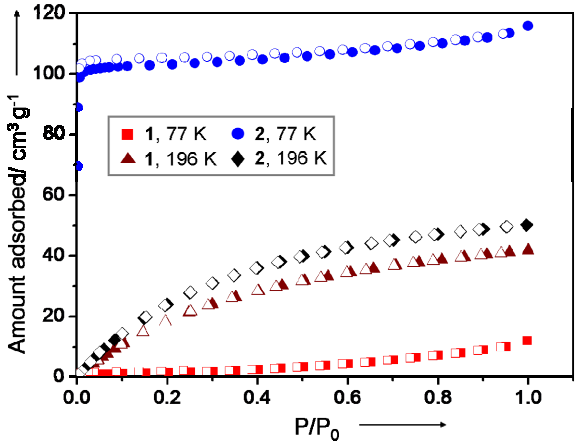

Figure S1. Nitrogen sorption isotherm for **1** and **2** (amount of gas adsorbed per gram adsorbent vs relative pressure): **1**, 77 K (squares), **1**, 196 K (triangles), **2**, 77 K (circles), **2**, 196 K (diamonds). Solid symbol = adsorption, open symbol = desorption

Table S1. Unit cell parameters and aperture sizes of $M(HCOO)_2$ (M = Mg, Mn)

T, K	*a*, Å	*b*, Å	*c*, Å	*β*, °	*V*, Å^3	aperture size[b], Å	
			$Mn(HCOO)_2$ (**1**)				
90[a]	11.719(1)	10.172(1)	14.920(1)	91.553(1)	1777.9(3)	3.64	This work
196[a]	11.732(1)	10.200(1)	14.947(1)	91.538(1)	1788.0(3)	3.66	This work
243	11.720(1)	10.207(1)	14.956(2)	91.538(1)	1788.6(3)	3.64	Ref.1
			$Mg(HCOO)_2$ (**2**)				
90[a]	11.341(1)	9.849(1)	14.547(1)	91.388(1)	1624.4(2)	3.36	This work
196[a]	11.359(1)	9.885(1)	14.584(1)	91.370(1)	1637.1(2)	3.38	This work
100	11.324(1)	9.847(2)	14.623(3)	91.150(3)	1630.2(6)	3.36	Ref.4

[a]X-ray diffraction data were collected on the same single crystal at different temperatures for each compound, [b]The diameter of the largest probe atom fitted to the narrowest part of the channel based on the crystal structure.

Table S2. Mean-square vibration amplitude (u^2) of atoms around the pore aperture of **1** and **2** by single-crystal X-ray analysis

atoms	u^2 (Å^2), (**1**)		u^2 (Å^2), (**2**)	
	90K	196K	90K	196K
C(1)	0.012(1)	0.018(1)	0.014(1)	0.019(1)
C(5)	0.014(1)	0.023(1)	0.015(1)	0.021(1)
C(6)	0.011(1)	0.021(1)	0.014(1)	0.018(1)

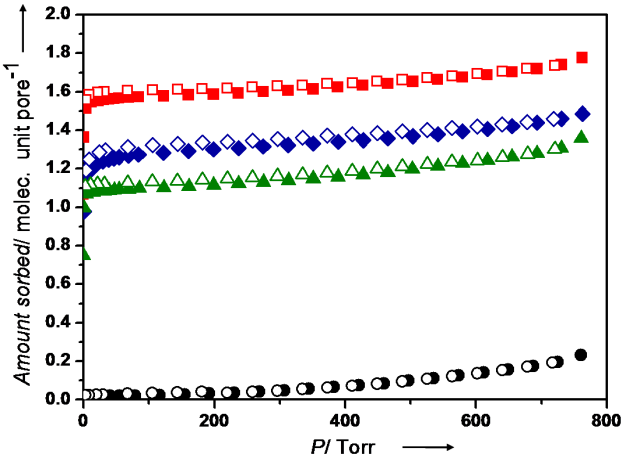

Figure S2. Nitrogen sorption isotherm for $M(HCOO)_2$ (M = Mg, Mn, Co and Ni) at 77 K: **1** (circles), **2** (squares), $Ni(HCOO)_2$ (diamonds) and $Co(HCOO)_2$ (triangles). Solid symbol = adsorption, open symbol = desorption.

Table S3. Aperture size of $M(HCOO)_2$ (M = Mn, Mg, Co, Zn and Fe)

$M(HCOO)_2$	Aperture size[a], Å
1	3.64 (90 K)
2	3.36 (90 K)
$Co(HCOO)_2$	3.28 (90 K)
$Zn(HCOO)_2$	3.32 (90 K)
$Fe(HCOO)_2$[3]	3.62 (105 K)

[a]The diameter of the largest probe atom fitted to the narrowest part of the channel based on the crystal structure.

References

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