

## Channel-Selective Independent Sorption and Collection of Hydrophilic and Hydrophobic Molecules by $\text{Cs}_2[\text{Cr}_3\text{O}(\text{OOCCH}_2\text{H}_5)_6(\text{H}_2\text{O})_3]_2[\alpha\text{-SiW}_{12}\text{O}_{40}]$ Ionic Crystal

Chunjie Jiang,<sup>†</sup> Aldes Lesbani,<sup>†</sup> Ryosuke Kawamoto,<sup>†</sup> Sayaka Uchida,<sup>†,‡</sup> and Noritaka Mizuno<sup>\*,†,‡</sup>

Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, 113-8656, Japan, and Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama, 332-0012, Japan

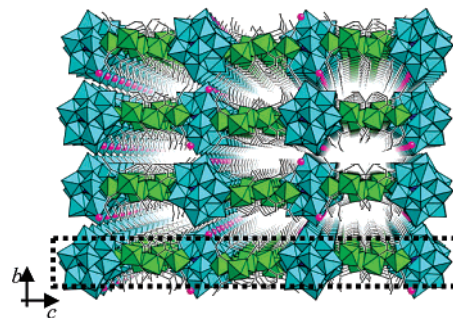
Received August 7, 2006; E-mail: tmizuno@mail.ecc.u-tokyo.ac.jp

Crystalline solids such as inorganic zeolites<sup>1</sup> and metal-organic frameworks (organic zeolites)<sup>2</sup> possess molecular-sized space and have received scientific interests because of their unique selectivity in the sorption, ion exchange, and catalysis. Crystalline solids possessing two or more distinct channels within the crystal lattice would realize the isolation and storage of mixtures and controlled reaction between two or more molecules. To date, there are only three examples of crystalline solids with two or more distinct channels, compounds of zinc-fluoropropylidene-benzoate,<sup>3a</sup> zinc-saccharate,<sup>3b</sup> and zinc-triazine-triphenylene.<sup>3c</sup> However, nothing is known of the channel-selective independent sorption and collection of hydrophilic and hydrophobic molecules.

Polyoxometalates are nanosized metal–oxygen macroanions and suitable building blocks of ionic crystals in combination with appropriate macrocations. Recently, we have reported the synthesis of an ionic crystal of  $\text{K}_2[\text{Cr}_3\text{O}(\text{OOCCH}_2\text{H}_5)_6(\text{H}_2\text{O})_3]_2[\alpha\text{-SiW}_{12}\text{O}_{40}]$  with hydrophilic and hydrophobic channels.<sup>4a</sup> The guest-free phase sorbs water while hydrophobic molecules are excluded probably because the opening of the hydrophobic channel is too small. On the basis of these results, we have reached an idea that the opening of the hydrophobic channel can be increased by changing  $\text{K}^+$  to larger alkali metal ions, and that the resulting guest-free phase shows the channel-selective sorption of hydrophilic and hydrophobic molecules. Here, we report that the guest-free phase of  $\text{Cs}_2[\text{Cr}_3\text{O}(\text{OOCCH}_2\text{H}_5)_6(\text{H}_2\text{O})_3]_2[\alpha\text{-SiW}_{12}\text{O}_{40}] \cdot 4\text{H}_2\text{O}$  [**1a**] sorbs dichloromethane and water in the hydrophilic and hydrophobic channels, respectively. The rate and equilibrium amount of the dichloromethane sorption into the hydrophobic channel and those of water into the hydrophilic channel were independent of each other. The sorption property can be applied to the collection of hydrophilic (water) and hydrophobic (dichloromethane) molecules from the mixture.

The water of crystallization in **1a** was removed by evacuation at 303 K to form the guest-free phase **1b**. The crystal structure of **1b** is shown in Figure 1. The Rietveld analysis of the XRD pattern showed the parameters of monoclinic  $C2/c$ ,  $a = 15.87$ ,  $b = 19.99$ ,  $c = 30.47$  Å,  $\beta = 90.22^\circ$  and  $V = 9667$  Å<sup>3</sup> (Figure S1). The layers were stacked along the  $b$ -axis, and cesium ions resided between adjacent layers. The straight hydrophobic channels surrounded by the propionate ligands of the macrocations existed between layers, and hydrophilic channels existed along the [110] direction through the layers. The volumes of the hydrophilic and hydrophobic channels of **1b** were 20 and 30  $\mu\text{L g}^{-1}$ , respectively. The narrowest and widest openings of the hydrophobic channel were 4.0 Å and 5.2 Å, respectively.

The amount of dichloromethane sorption increased with the increase in the vapor pressure at 273 K and reached 23  $\mu\text{L g}^{-1}$



**Figure 1.** Crystal structure of **1b**. Blue, light blue, and green polyhedra showed the  $[\text{SiO}_4]$ ,  $[\text{WO}_6]$ , and  $[\text{CrO}_6]$  units, respectively. Black sticks showed the propionate ligand. Pink spheres showed the cesium atoms. The dotted rectangle showed the layer.

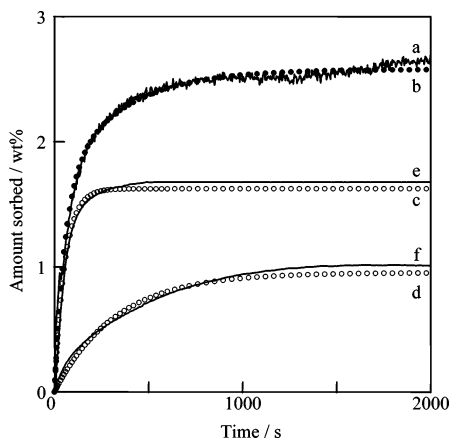
(1.6 mol mol<sup>-1</sup>) at  $P/P_0 = 0.94$  (Figure S2).<sup>6</sup> The amount of sorption at 298 K in the  $P/P_0$  range of 0–0.85 was almost the same as that at 273 K. The changes in the amounts of dichloromethane sorption by **1b** as a function of time at  $P/P_0 = 0.40$  (298 K) were reproduced with a single rate constant<sup>6</sup> ( $k_1 = 2.6 \times 10^{-3} \text{ s}^{-1}$  and  $M_{e1} = 7.6 \mu\text{L g}^{-1}$ , Figure S3b) and similar results were obtained at  $P/P_0 = 0.60$ , showing that a single barrier existed for the sorption. The amount of dichloromethane sorption by **1b** at  $P/P_0 = 0.60$  (298 K) upon the presorption of water ( $22 \pm 1 \mu\text{L g}^{-1}$ ,  $5.5 \pm 0.2 \text{ H}_2\text{O}$  per **1b**) was  $9.3 \pm 0.5 \mu\text{L g}^{-1}$  ( $0.66 \pm 0.03 \text{ CH}_2\text{Cl}_2$  per **1b**) and fairly agreed with that  $10 \pm 0.5 \mu\text{L g}^{-1}$  without the pretreatment (Scheme 1). The opening of the hydrophobic channel in **1b** was comparable to the diameter of the dichloromethane molecule (4.2 Å). These facts show that dichloromethane is accommodated into the hydrophobic channel in **1b** and that the amount is not influenced by the presorption of water.

The amount of water sorption by **1b** increased with the increase in the vapor pressure, and the amount reached  $22 \pm 1 \mu\text{L g}^{-1}$  at  $P/P_0 = 0.90$  (Figure S2) and was close to the volume of the hydrophilic channel (20  $\mu\text{L g}^{-1}$ ). The water sorption could be reproduced with a single rate constant<sup>7</sup> and  $k_1 = 1.5 \times 10^{-2} \text{ s}^{-1}$  and  $M_{e1} = 16.6 \mu\text{L g}^{-1}$  gave the best fits at  $P/P_0 = 0.60$  (Figure S3a). Therefore, that a single barrier exists for the water sorption is in accord with the idea that water resides only in the hydrophilic channel. Thus, compound **1b** possesses hydrophobic and hydrophilic channels and dichloromethane and water are sorbed in the respective channels.

Next, the effect of the existence of water vapor on the sorption of dichloromethane by **1b** was investigated.<sup>7</sup> When **1b** was exposed to a gas flow (He balance) containing water ( $P/P_0 = 0.60$ ) and dichloromethane ( $P/P_0 = 0.40$ ), the weight increased as shown in Figure 2. The best fits for the experimental data were given by  $k_1 = 1.7 \times 10^{-2} \text{ s}^{-1}$ ,  $M_{e1} = 16.4 \mu\text{L g}^{-1}$  (1.64 wt %),  $k_2 = 3.0 \times$

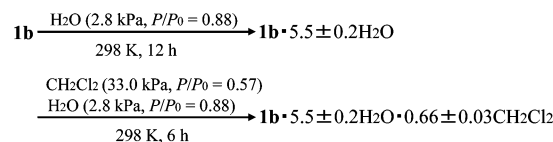
<sup>†</sup> The University of Tokyo.

<sup>‡</sup> Japan Science and Technology Agency (JST).

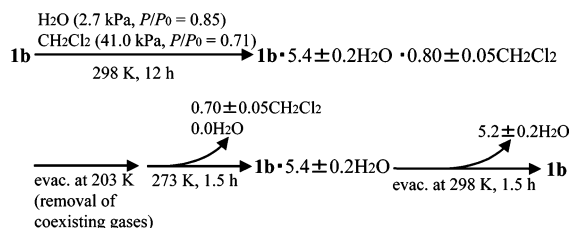


**Figure 2.** Changes in the weight of **1b** by the exposure to a gas mixture of water ( $P/P_0 = 0.60$ ) and dichloromethane ( $P/P_0 = 0.40$ ) at 298 K. Solid line a showed the experimental data. Solid lines e and f showed the experimental sorption data of water ( $P/P_0 = 0.60$ , Figure S3a) and dichloromethane ( $P/P_0 = 0.40$ , Figure S3b), respectively. Solid circles b showed the calculated data (see Supporting Information), and open circles showed the two components for the calculation; (c)  $k_1 = 1.7 \times 10^{-2} \text{ s}^{-1}$  and  $M_{e1} = 16.4 \mu\text{L g}^{-1}$ ; (d)  $k_2 = 3.0 \times 10^{-3} \text{ s}^{-1}$  and  $M_{e2} = 7.0 \mu\text{L g}^{-1}$ .

#### Scheme 1



#### Scheme 2



$10^{-3} \text{ s}^{-1}$ , and  $M_{e2} = 7.0 \mu\text{L g}^{-1}$  (0.93 wt %). The  $k_1$  and  $M_{e1}$  values were close to those of water sorption at  $P/P_0 = 0.60$  and the  $k_2$  and  $M_{e2}$  values were close to those of dichloromethane sorption at  $P/P_0 = 0.40$ . Therefore, the rate and equilibrium amount of the dichloromethane sorption into the hydrophobic channel and those of water into the hydrophilic channel of **1b** were independent of each other, and the phenomenon was different from those of zeolites and activated carbons, of which the amounts of dichloromethane sorption are decreased by the presence of water.<sup>9</sup>

Finally, the collection of dichloromethane and water from the gas mixture was attempted according to Scheme 2. Compound **1a** was evacuated at 298 K for 6 h to form **1b** followed by the exposure to the gas mixture of water ( $P/P_0 = 0.85$ ) and dichloromethane ( $P/P_0 = 0.71$ ) at 298 K for 12 h to form  $\mathbf{1b} \cdot (5.4 \pm 0.2)\text{H}_2\text{O} \cdot (0.80 \pm 0.05)\text{CH}_2\text{Cl}_2$ . After the removal of the coexisting gases, the sample was heated at 273 K and kept for 1.5 h. The amount of dichloromethane evolved was  $9.9 \pm 0.5 \mu\text{L g}^{-1}$  ( $(0.70 \pm 0.05)\text{CH}_2\text{Cl}_2$  per **1b**). Then the sample was evacuated at 298 K for 1.5 h and the amount of water collected was  $22 \pm 1 \mu\text{L g}^{-1}$  ( $(5.2 \pm 0.2)\text{H}_2\text{O}$  per **1b**). Thus, dichloromethane and water sorbed in **1b** were successfully collected.

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of Japan. C.J. and R.K. are grateful to JBIC and JSPS, respectively, for financial supports.

**Supporting Information Available:** Experimental details and syntheses. Figures S1–S3 show powder XRD patterns of **1a** and **1b**, the sorption isotherms of **1b**, and changes in the amounts of sorption for **1b** with the exposure to water and dichloromethane vapors, respectively; crystallographic data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- The Rietveld analysis of powder XRD of **1a** (Figure S1) showed the parameters of monoclinic  $C2/c$ ,  $a = 16.26$ ,  $b = 20.19$ ,  $c = 30.30 \text{ \AA}$ ,  $\beta = 90.63^\circ$  and  $V = 9943 \text{ \AA}^3$ . The calculated pattern well reproduced the experimental pattern. Compound **1a** showed two-step weight losses of water of 1.64% and 2.43% below 373 K and in the range of 383–433 K, respectively. The respective values agreed with 1.61% (4 mol mol<sup>-1</sup>) of the water of crystallization and 2.36% (6 mol mol<sup>-1</sup>) of the water ligands of the macrocation. The nitrate salt of the macrocation showed a weight loss of 7.50% in the range of 383–433 K, which fairly agreed with 7.44% of the water ligands, supporting the assignment. The in situ XRD patterns showed that the lattice parameters did not much change ( $\pm 2\%$  lattice volume change) in the range of 298–473 K and that the pattern after the treatment at 473 K reversibly changed to that of **1a** upon the exposure to water vapor at 298 K.
- Compound **1b** sorbed dichloromethane (molecular area  $0.244 \text{ nm}^2$ ) and 1,2-dichloroethane ( $0.277 \text{ nm}^2$ ), while chloroform ( $0.283 \text{ nm}^2$ ) and 1,2-dichloropropane ( $0.324 \text{ nm}^2$ ) were excluded.
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