# Zeotype Ionic Crystal of Cs$_5$[Cr$_3$O(OOCH)$_6$(H$_2$O)$_3$][α-CoW$_{12}$O$_{40}$]·7.5H$_2$O with Shape-Selective Adsorption of Water

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The design and syntheses of new crystalline microstructured solid-state materials such as zeolites and their analogues have attracted much attention because of their guest inclusion properties.[1,2] Aluminosilicate zeolites and their inorganic analogues with well-defined micropores show shape-selective adsorption and catalysis and have been most widely applied to the separation of C4 alkanes,[3,4] oxygen from air,[5] and water from an azeotropic mixture of water and ethanol (bp 351 K at 4.00 wt % of H$_2$O).[6] There is also a great interest in the syntheses of organic zeolites with organic or organometallic building blocks.[2,7] These organic zeolites can be easily functionalized at atomic and molecular levels and show unique inclusion properties. Even inorganic and organic zeolites cannot shape-selectively distinguish water from methanol and ethanol.

Nanosized polyoxometalates are also suitable building blocks for crystalline microstructured materials,[8] and some compounds contain nitriles or alcohols as guests[9] though they cannot be removed or reversibly included. Recently, we have reported the synthesis of K$_3$[Cr$_3$O(OOCH)$_6$ (H$_2$O)$_3$][α-SiW$_{12}$O$_{40}$]·16H$_2$O and the selective inclusion of polar molecules up to C2. The inclusion property was quantitatively explained by the change in the lattice energy associated with the structural change of the host in the guest sorption−desorption.[10,11] On the basis of the results, we reached an idea that the cation−anion interaction increases with an increase in the anion charges, and the closer packing of the ions is achieved to reduce the size and space for the polar guests. The reduction will lead to the shape-selective adsorption and separation. Here, we report a zeotype polyoxometalate-macrocation ionic crystal of Cs$_5$[Cr$_3$O(OOCH)$_6$(H$_2$O)$_3$][α-CoW$_{12}$O$_{40}$]·7.5H$_2$O (**1a**) with the shape-selective adsorption of water and separation of only water from an ethanol/water azeotropic mixture.

The schematic illustration of the synthesis and the crystal structure[12] (*ab* plane) of **1a** are shown in Figure 1. The polyoxometalates and macrocations were alternatively arranged, and the surplus anion charges were compensated by the neighboring cesium ions. The space volume of **1a** corresponded to 17% of the crystal lattice and was smaller than 36% of K$_3$[Cr$_3$O(OOCH)$_6$(H$_2$O)$_3$][α-SiW$_{12}$O$_{40}$]·16H$_2$O with polyoxometalate charge of −4. The water of crystallization in **1a** was closely located (O$_w$−O$_w$: 2.72−2.77 Å) to form a winding hydrogen bond network along the *a*-axis (Figure 1B). These water molecules were surrounded by the constituent ions (Cs$^+$−O$_w$: 2.30−2.78 Å, O$_{macro}$−O$_w$: 2.59−2.76 Å, O$_{poly}$−O$_w$: 2.85−3.10 Å). The narrowest cross diameter of the channel was ca. 2.7 Å and comparable to the van der Waals diameter of oxygen (3.0 Å).[13]

About 50% of the water of crystallization in **1a** was desorbed by the evacuation at room temperature to form phase **1b** (weight loss 1.8 wt %, calcd 1.7 wt % for the desorption of 4 mol of the water of crystallization per mol of [α-CoW$_{12}$O$_{40}$],$^{6-}$ i.e., there are ca. 3.5 mol left in **1b**). The sample **1b** for the single-crystal analysis
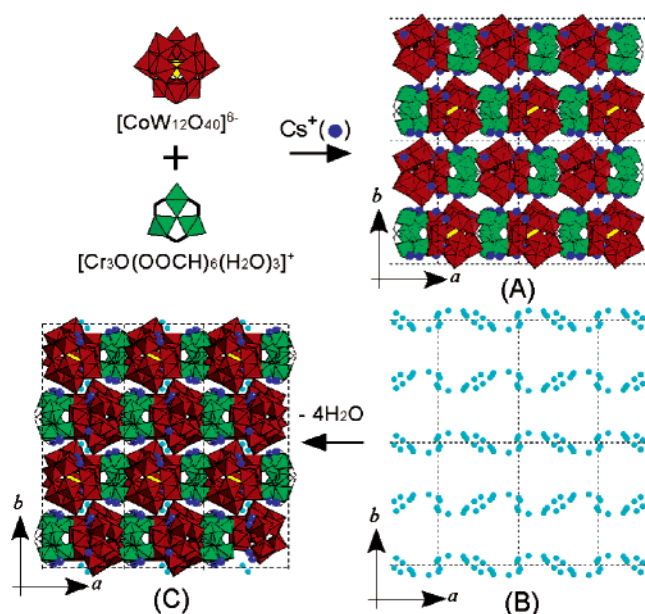


***Figure 1.*** Synthesis and crystal structure (*ab* plane) of **1a** and **1b**. Location of the (A) constituent ions and (B) water of crystallization in **1a**. (C) **1b**.

was prepared by the dehydration of the single crystal of **1a** under a dry N$_2$ flow (333 K, 3 h). Then the crystal structure of **1b** was determined. The crystal structure is shown in Figure 1C.[14] The arrangements of the polyoxometalates and macro cations were essentially the same as those in **1a**, while small reduction in the *a*- (−0.316 Å) and *b*-axes (−0.696 Å) of the lattice was observed. The position of two molecules of the water of crystallization in **1b** could be crystallographically determined. These water molecules were coordinated to the cesium ions (Cs$_1$$^+$−O$_{w1}$: 3.04 Å, Cs$_2$$^+$−O$_{w2}$: 3.03 Å), were crystallographically different, and were not in hydrogen-bonding distance (O$_{w1}$−O$_{w2}$: 5.13 Å).

The states of the water of crystallization in **1a** and **1b** were supported by the in situ IR measurements. The IR spectrum of **1a** showed a broad band around 2500−3600 cm$^{-1}$, assignable to the ν(OH) band of the water molecules with hydrogen bonding.[15] On the other hand, the IR spectrum of **1b** showed two sharp bands at 3570 and 3450 cm$^{-1}$ with the integrated intensity ratio of 1:1. Therefore, the bands at 3570 and 3450 cm$^{-1}$ were assigned to the water of crystallization coordinated to Cs$^+$, taking into account the crystallographic data and the report that water molecules adsorbed on alkali metal ion exchanged zeolites (<1 molecule/alkali metal ion) show the sharp ν(OH) bands around 3500 cm$^{-1}$.[15] The powder XRD pattern of **1a** and **1b** showed reversible transformation between **1a** and **1b** without the changes in the intensity and half-width of the signals upon the water sorption−desorption cycles (Figure S1).
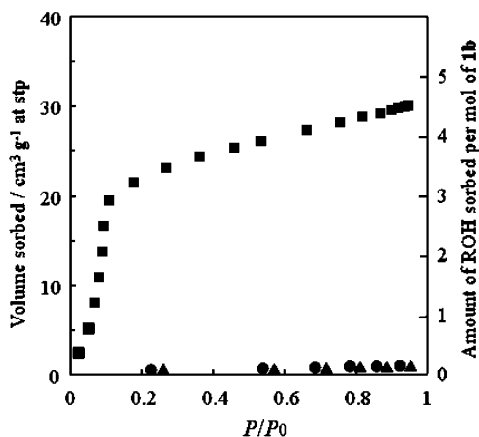
**Figure 2.** Water (■, $P_o$ = 3.06 kPa), methanol (●, $P_o$ = 15.6 kPa), and ethanol (▲, $P_o$ = 6.67 kPa) sorption isotherms of **1b** at 298 K.

Next, the guest inclusion properties of **1b** were investigated. Figure 2 shows the water, methanol, and ethanol sorption isotherms for **1b** at 298 K. The amount of water uptake sharply increased in the low relative pressure, and the shape of the isotherm can be categorized as type I, characteristic of the guest sorption into the micropores.[16] On the other hand, the amounts of methanol (1.5 cm³ g⁻¹ at $P/P_o$ = 0.9) and ethanol (1.4 cm³ g⁻¹ at $P/P_o$ = 0.9) sorption were close to or smaller than those for the surface adsorption (~2 cm³ g⁻¹) and were negligible. Therefore, **1b** could adsorb water molecules (molecular area:[17] 10.5 Å²) but excluded larger methanol (17.9 Å²) and ethanol (23.0 Å²). The water molecules probably diffused into the winding hydrophilic channels, slightly expanding the *a*- and *b*-axes of the lattice. Thus, it was demonstrated that **1b** can shape-selectively and reversibly adsorb water molecules without the essential change of the crystal structure.

The water inclusion property of **1b** was applied to the removal of water from highly pure ethanol. The compound **1b** included only water, and the concentration was decreased from 0.23 wt % to 0.08 wt % at 298 K (Figure S2). The value of 0.08 wt % is below the limit (<0.1 wt %) of anhydrous ethanol.[18] Lowering the sorption temperature to 273 K further decreased the water content to 0.06 wt %. The compound **1b** could be recycled only by the separation from the ethanol solution with decantation, followed by the evacuation at room temperature. The amount of removed water remained unchanged even after six cycles, and **1b** could be easily recyclable (Figure S4). The compound **1b** also included only water from the water (0.1–0.2 M)/ethanol (0.1–0.2 M)/1-propanol (ca. 13 M) mixture.

**Supporting Information Available:** Experimental details and synthesis of **1a** and **1b**. Table S1 summarizes the data for water and ethanol sorption from the azeotropic mixture at 298 K. Figure S1 shows the in situ powder XRD pattern of **1a** and **1b** under controlled water vapor flow. Figure S2 shows the changes in the water concentration in highly pure ethanol by the addition of MS-3A and **1b**. Figure S3 shows the recycling of **1b** for the removal of water. Figure S4 shows the plots of ln(1 − $Q_t/Q_\infty$) vs time for the water sorption by MS-3A or **1b** (PDF).

X-ray crystallographic files of **1a** and **1b** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Crystal data for Cs₅[Cr₃O(OOCH)₆(H₂O)₃][α-CoW₁₂O₄₀]·7.5H₂O (**1a**), $M_w$ = 4173.68, monoclinic, space group $P2_1/c$, *a* = 12.642(3), *b* = 19.337-(5), *c* = 24.341(6), *β* = 89.644(4), *V* = 5950.4(23), *T* = 123.1 K, *Z* = 4, $R_1$ = 0.0450, w$R_2$ = 0.0560.

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(14) Crystal data for Cs₅[Cr₃O(OOCH)₆(H₂O)₃][α-CoW₁₂O₄₀]·2H₂O (**1b**), $M_w$ = 4085.68, monoclinic, space group $P2_1/c$, *a* = 12.3267(11), *b* = 18.641-(2), *c* = 24.487(3), *β* = 92.332(2), *V* = 5622.0(10), *T* = 303.1 K, *Z* = 4, $R_1$ = 0.093, w$R_2$ = 0.115.

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(17) The molecular area was calculated from the molecular weight and density of liquid at 298 K.

(18) The amounts of water in the ethanol solution were decreased to 0.14 wt % and 0.17 wt % by the addition of MS-3A or MS-4A at 298 K, respectively. The diffusion coefficients for the absorption of water for **1b** and MS-3A were 1.1 × 10⁻¹⁴ and 2.7 × 10⁻¹⁵ cm² s⁻¹, respectively (Figure S3).[19] MS-3A also adsorbed almost the same amount of ethanol as that of water. In the case of MS-4A, the amount of ethanol adsorbed was 6 times larger than that of water adsorbed (Table S1).

(19) The diffusion coefficient for the adsorption of water on MS-4A in water/2-propanol mixture was reported to be 4 × 10⁻¹³ cm² s⁻¹ [20] while those values for MS-3A or 4A in pure water were in the range of 10⁻⁵ to 10⁻⁷ cm² s⁻¹ and larger.[21,22] The decrease in the diffusion coefficient in the presence of 2-propanol was probably because coexisting 2-propanol absorbed inside the micropore of the zeolites prohibited the diffusion of water. In the present case, the plots of the amount of water adsorbed on MS-4A in ethanol solution did not obey the equation of $Q_t/Q_\infty = 1 − (6/\pi^2)\exp(−D\pi^2t/r^2)$,[23] and the diffusion coefficient could not be calculated.

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