

12. Muscatello, A. C.; Choppin, G. R.; D'Olieslager, W. *Inorg. Chem.* **1989**, *28*, 993.
13. Wilkins, R. G. *The Study of Kinetics and Mechanisms of Reactions of Transition Metal Complexes*; Allyn and Bacon, Inc.: Boston, 1974; Chap. 1.
14. Kasprzyk, S. P.; Wilkins, R. G. *Inorg. Chem.* **1982**, *21*, 3349.
15. Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum Press: New York, 1989; Vol. 6.
16. DeJongh, M.; D'Olieslager, W. *Inorg. Chim. Acta.* **1985**, *109*, 7.
17. Choi, K. Y.; Kim, K. S.; Kim, J. C. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 267.
18. Choi, K. Y.; Choppin, G. R. *Inorg. Chem.* submitted for publication.
19. Choi, K. Y.; Choppin, G. R. *J. Coord. Chem.* **1991**, *24*, 19.

Crystal Structures of Zeolitic Water Molecules in Cs₃Na₉-A and Cs₃Na₈H-A

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Received December 2, 1993

Structures of zeolitic water molecules in hydrated Cs₃Na₉-A and Cs₃Na₈H-A have been studied by single-crystal x-ray diffraction methods in the cubic space group $Pm\bar{3}m$ at 21°C. In the crystal structure of fully dehydrated Cs₃Na₉-A ($a = 12.265(1)$ Å with $R_1 = 0.056$ and $R_2 = 0.057$), nearly three and eight Cs⁺ and Na⁺ ions per unit cell are found at the centers of 8- and 6-oxygen rings with closest approaches of 3.401(11) and 2.303(6) Å to framework oxygens, respectively. The twelfth Na⁺ is located opposite 4-oxygen ring in the large cavity with an occupancy of 0.6(2). The crystal structures of hydrated Cs₃Na₉-A ($a = 12.273(1)$ Å with $R_1 = 0.065$ and $R_2 = 0.078$) and Cs₃Na₈H-A ($a = 12.286(1)$ Å with $R_1 = 0.078$ and $R_2 = 0.081$) are viewed as having two kinds of unit cells, Cs₃Na_{9-x}H_x-A·20H₂O and Cs₃Na_{9-x}H_x-A·24H₂O ($x = 0$ and 1, respectively), each with different secondary structures of zeolitic water molecules in its large cavity. In both unit cells, Cs⁺ ions are found at centers of 8-rings with large thermal parameters, showing changes in their coordination environments due to approaches of water molecules upon hydration. Na⁺ ions on 6-rings have also changed their geometries from trigonal to tetrahedron upon hydration, each with three framework oxygens at 2.356(11) Å and an additional zeolitic water molecule at 2.18(3) Å on a threefold axis which is perpendicular to the 6-ring of the framework oxygens. In the large cavity of Cs₃Na_{9-x}H_x-A·20H₂O, four water molecules are arranged tetrahedrally on the threefold axes, each in turn with tetrahedrally coordinated three water molecules at 2.83(6) Å. In the case of Cs₃Na_{9-x}H_x-A·24H₂O, eight water molecules on the threefold axes occupy eight symmetry equivalent positions, each in turn with tetrahedrally coordinated three waters at 2.51(6) Å, resulting in a pseudo-dodecahedron of twenty water molecules with twelve shared and distorted pentagons perturbed by approaches of Cs⁺ ions. Four water molecules in each sodalite unit of both crystals are arranged tetrahedrally and seem to have weaker interactions with the Na⁺ ions on 6-rings due to the stronger interactions between the Na⁺ ions and the water molecules in the large cavity.

Introduction

Unlike other guest molecules in the molecular-dimensioned cavities of zeolites, water molecules tend to make bonds to both exchangeable cations and framework oxide anions by donating lone-pair electrons to the empty orbitals of cations and hydrogens to the framework oxide anions, respectively. Accordingly, their distances from cations and framework atoms are limited within their normal and hydrogen bonding distances, especially when they are located within the primary coordination spheres of the zeolitic cations and framework atoms. Such zeolitic water molecules are some-

times found to be a part of secondary and tertiary structures, which are usually found in the molecular-dimensioned channels and cavities with appropriate volumes.^{1,2} As stable secondary structures suggested by many theoretical chemists,^{3,4} pentagons of water molecules were actually found crystallographically in narrow hydrophilic regions of hydrophobic protein¹ as well as in the cavities of zeolite A.² Helical arrangement of water molecules was also reported in the channels of hydrated VPI-5 zeolite.⁵ However, the presence of tertiary structures of water molecules, such as helical strands and dodecahedron, is so far suggested only in the highly symmetrical channels and cavities of hydrated zeolites.^{2,5}

The presence of dodecahedron of water molecules, consisting of twelve pentagons with twenty water molecules, in the large cavity of hydrated $\text{Na}_{12}\text{-A}$ had been reported by Gramlich and Meier.² However, the suggested dodecahedron can not be considered as a crystallographically noble one because of partial occupancies and modified positions of some water molecules for the suggested tertiary structure. Furthermore, not all of the cations, which seem to play important roles in locating and arranging water molecules in the cavity, are identified and some of them (four out of twelve Na^+ ions per $\text{Pm}\bar{3}\text{m}$ unit cell) were actually treated as water molecules in the course of crystallographic refinements.²

In this study, we attempted to investigate the structures of zeolitic water molecules in the cavities of hydrated zeolite A by replacing three Na^+ ions, unidentified in the previous structure,² with Cs^+ ions at the centers of 8-ring ((0, 1/2, 1/2) with a point symmetry of 4/mmm in the unit cell of $\text{Pm}\bar{3}\text{m}$) in order to prevent uncertainty raised by Na^+ ions at usual less-symmetrical positions (with a point symmetry of mm). The correct positions of water molecules in the cavity will be crucial in the crystallographic identification of them from different guest molecules, introduced by other physico-chemical methods,⁶⁻⁸ especially when the zeolites have possibilities of containing not-dehydrated or scavenged water molecules.

Experimental

Colorless crystals of $\text{Na}_{12}\text{Si}_{12}\text{Al}_{12}\text{O}_{48} \cdot 27\text{H}_2\text{O}$ ($\text{Na}_{12}\text{-A} \cdot 27\text{H}_2\text{O}$)⁹ were prepared by Charnell's method.¹⁰ Ion-exchanges of Cs^+ ions into the zeolites were carried out dynamically (flowing stream) at 20°C for five days with 0.1 N aqueous solutions of 30 mol% Cs^+ , made of CsOH and NaOH (pH=11.7) and of CsNO_3 and NaNO_3 (pH=5.7) for $\text{Cs}_3\text{Na}_9\text{-A}$ and $\text{Cs}_3\text{Na}_6\text{H-A}$, respectively (*vide infra*). These solution compositions were chosen so that all 8-ring sites would be occupied by Cs^+ ions.¹¹ All reagents used for the ion-exchange were ultra pure (both 99.99% from Sigma and Aldrich Chemical Co.).

A single crystal of hydrated $\text{Cs}_3\text{Na}_9\text{-A}$, a cube 80 μm on an edge, was lodged in fine Pyrex capillary on a vacuum line for dehydration, so that the structures of framework itself and cations of the zeolite can be examined first (crystal 1). After cautious increases of temperature with 25°C/h and following complete dehydration at 350°C and 5×10^{-6} Torr for four days, the crystal-containing capillary still under vacuum were sealed off from the vacuum line at room temperature. Single crystals of hydrated $\text{Cs}_3\text{Na}_9\text{-A}$ and $\text{Cs}_3\text{Na}_6\text{H-A}$ (crystals 2 and 3, respectively) are dried in the air and they still in the ion-exchange capillaries were sealed off in order to maintain a constant humidity during the course of x-ray experiments. No changes were noted in the appearance of the crystals upon the ion-exchange and dehydration.

The cubic space group $\text{Pm}\bar{3}\text{m}$ (no systematic absences) was used throughout this work for reasons discussed previously.^{6,12-13} A computer-controlled CAD4/Turbo diffractometer equipped with a rotating anode generator and a graphite monochromator was used for preliminary experiments and for the subsequent collection of diffraction intensities, all at 21(2)°C. Molybdenum radiation ($K\alpha_1$, $\lambda=0.70930$ Å; $K\alpha_2$, $\lambda=0.71359$ Å) was used. In each case, the cell constant, $a=12.265(1)$, $12.273(1)$, and $12.286(1)$ Å, for crystals 1 to 3, res-

pectively, was determined by a least-squares treatment of 15 intense reflections for which $20 < 2\theta < 30^\circ$. The ω - 2θ scan technique was used for data collection in a region of reciprocal space (hkl , $h \leq k \leq l$) with additional data from two more intensity-equivalent regions (hkl , $l \leq h \leq k$; hkl , $h \leq l \leq k$) for hydrated $\text{Cs}_3\text{Na}_9\text{-A}$ (crystal 2). Each reflection was scanned at a constant scanning speed of 0.5°/min in 2θ with scan widths of $(0.48 + 0.68 \cdot \tan\theta)$, $(0.48 + 0.55 \cdot \tan\theta)$, and $(0.56 + 0.79 \cdot \tan\theta)^\circ$, for crystals 1 to 3, respectively. Background intensity was counted at each end of a scan range for a time equal to half the scan time. The intensities of three reflections in diverse regions of reciprocal space were recorded every three hours to monitor crystal and instrumental stability. Only small random fluctuations of these check reflections were observed during the course of data collection. The intensities of all lattice points for which $2\theta < 70^\circ$ were recorded.

For all three crystals, the raw intensities were calculated as $I_{\text{raw}} = \text{ATN} \cdot (C - R \cdot B) / \text{NPI}$, where C =total count, R =ratio of scan time to background counting time (2.0), B =total background count, NPI =ratio of fastest possible scan rate to scan rate for the each measurement, and ATN =attenuation factor, respectively. The observed structure factor amplitude of each reflection (F_o) was then obtained as the square root of the I_{raw} after correction for Lorentz-polarization (L_p): the contribution of the monochromator crystal was calculated assuming it to be half-perfect and half-mosaic in character. Standard deviations ($\sigma(F_o)$) of observed structure factors were assigned to individual reflections by the formula, $(\sigma(I)^2 + (pF_o^2))^{1/2} / 2F_o$. $\sigma(I)$ is standard deviation, based on counting statistics, of I_{raw} . The value $p=0.04$ was found to be appropriate for the instrumentation used. The data from the intensity-equivalent regions of hydrated $\text{Cs}_3\text{Na}_9\text{-A}$ (crystal 2) were merged with MolEN.¹⁴ Absorption correction (μR ca. 0.18 for all three crystals¹⁵) were judged to be negligible for all crystals, as shown in semi-empirical ψ -scans of dehydrated $\text{Cs}_3\text{Na}_6\text{H-A}$.⁶ Only those reflections in each final data set for which the net count exceeded three times its standard deviation were used in structure solution and refinement. This amounted to 254, 251, and 179 reflections for crystals 1 to 3, respectively.

Structure Determination

Dehydrated $\text{Cs}_3\text{Na}_9\text{-A}$ (crystal 1). Full-matrix least-squares refinement¹⁴ was commenced using the atomic parameters of all framework atoms [(Si, Al), O(1), O(2), and O(3)] and Cs^+ at Cs(1) and Na^+ at Na(1) in dehydrated $\text{Cs}_3\text{Na}_6\text{H-A}$.⁶ The refinement with anisotropic thermal parameters of all atoms converged quickly to error indices of $R_1 = \Sigma |F_o - |F_c|| / \Sigma F_o = 0.0535$ and $R_2 = (\Sigma w(F_o - |F_c|)^2 / \Sigma w F_o^2)^{1/2} = 0.0510$ with occupancies of 2.87(1) and 8.3(1) for Cs(1) and Na(1), respectively. A peak found opposite a 4-ring of large cavity (0.23, 0.23, 0.5) in a Fourier difference function prepared with this model was introduced as Na^+ at Na(2) with an isotropic thermal parameter. A subsequent least-squares refinement with this model resulted in occupancy of 0.6(2) with unrealistic thermal parameter for Na(2). When a fixed thermal parameter of 10.0 Å² for the Na(2) is used, the same refinement converged to the error indices of $R_1=0.0539$ and $R_2=0.0553$ with occupancies of 2.87(2), 8.1(1), and 0.6(2) for Cs(1), Na(1) and Na(2), respectively. The final cycles of refinement with

Table 1. Positional, Thermal, and Occupancy Parameters^a

Wyckoff											Occupancy ^d	
Position		<i>x</i>	<i>y</i>	<i>z</i>	β_{11} ^b or B_{130} ^c	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	fixed	varied
(a) Dehydrated Cs ₃ Na ₉ -A, crystal 1												
(Si,Al)	24(<i>k</i>)	0	1832(2)	3714(2)	20(1)	16(1)	12(1)	0	0	4(3)	24 ^e	
O(1)	12(<i>h</i>)	0	2227(8)	5000 ^f	53(8)	53(8)	12(6)	0	0	0	12	
O(2)	12(<i>i</i>)	0	2954(6)	2954(6)	63(8)	30(4)	30(4)	0	0	45(11)	12	
O(3)	24(<i>m</i>)	1119(3)	1119(3)	3396(5)	35(3)	35(3)	36(5)	12(8)	−4(6)	−4(6)	24	
Na(1)	8(<i>g</i>)	2029(4)	2029(4)	2029(4)	59(3)	59(3)	53(3)	53(3)	53.3(3)	53(3)	8.1(1)	
Cs(1)	3(<i>c</i>)	0	5000 ^f	5000 ^f	104(3)	82(1)	82(1)	0	0	0	2.87	2.87(2)
Na(2)	12(<i>l</i>)	2311(134)	2311(134)	5000 ^f	10.0 ^g						0.6(2)	0.6(2)
(b) Hydrated Cs ₃ Na ₉ -A, crystal 2												
(Si,Al)	24(<i>k</i>)	0	1836(2)	3709(2)	19(1)	13(1)	8(1)	0	0	8(3)	24 ^e	
O(1)	12(<i>h</i>)	0	2236(8)	5000 ^f	76(9)	20(7)	14(6)	0	0	0	12	
O(2)	12(<i>i</i>)	0	2931(6)	2931(6)	52(8)	20(4)	20(4)	0	0	29(12)	12	
O(3)	24(<i>m</i>)	1129(4)	1129(4)	3400(6)	32(3)	32(3)	49(6)	14(9)	17(7)	17(7)	24	
Na(1)	8(<i>g</i>)	2171(10)	2171(10)	2171(10)	215(4)	215(4)	215(4)	403(9)	403(9)	403(9)	8	
Cs(1)	3(<i>c</i>)	0	5000 ^f	5000 ^f	563(15)	119(3)	119(3)	0	0	0	2.87	2.76(2)
O(4)	24(<i>m</i>)	2657(21)	2657(21)	4638(31)	6.86						6	6.5(4)
O(5)	8(<i>g</i>)	3199(19)	3199(19)	3199(19)	14.09						6	5.2(4)
O(6)	24(<i>l</i>)	2226(61)	3551(45)	5000 ^f	16.04						6	7.0(8)
O(7)	8(<i>g</i>)	900(38)	900(38)	900(38)	36.07						4	4.3(4)
(c) Hydrated Cs ₃ Na ₈ H-A, crystal 3												
(Si,Al)	24(<i>k</i>)	0	1837(4)	3712(4)	16(2)	13(2)	9(2)	0	0	12(6)	24 ^e	
O(1)	12(<i>h</i>)	0	2250(13)	5000 ^f	64(15)	15(11)	4(10)	0	0	0	12	
O(2)	12(<i>i</i>)	0	2936(9)	2936(9)	47(14)	10(7)	10(7)	0	0	11(19)	12	
O(3)	24(<i>m</i>)	1130(6)	1130(6)	3403(9)	33(6)	33(6)	43(10)	22(16)	35(11)	35(11)	24	
Na(1)	8(<i>g</i>)	2135(17)	2135(17)	2135(7)	271(7)	271(7)	271(7)	510(16)	510(16)	510(16)	8	
Cs(1)	3(<i>c</i>)	0	5000 ^f	5000 ^f	549(23)	117(5)	117(5)	0	0	0	2.86	2.83(3)
O(4)	24(<i>m</i>)	2754(33)	2754(33)	4631(42)	5.01						6	6.3(5)
O(5)	8(<i>g</i>)	3241(28)	3241(28)	3241(28)	13.38						6	5.6(4)
O(6)	24(<i>l</i>)	2180(72)	3678(60)	5000 ^f	10.45						6	5.2(6)
O(7)	8(<i>g</i>)	852(48)	852(48)	852(48)	25.11						4	4.0(3)

^aPositional and anisotropic thermal parameters are given $\times 10^4$. Numbers in parentheses are the estimated standard deviations in the units of the least significant figure given for the corresponding parameter. The anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. ^bR. m. s. displacements can be calculated from β_{ii} values using formula $\mu_i = 0.255 a(\beta_{ii})^{1/2}$, where $a = 12.260$ Å. ^cIsotropic thermal parameter in units of Å². ^dOccupancy factors are given as the number of ions per unit cell. ^eOccupancy for (Si)=12, occupancy for (Al)=12. ^fExactly 1/2 by symmetry. ^gThis parameter was fixed in the final least-squares refinement.

fixed occupancies of 2.87 and 8.0 (its maximum value by symmetry) for Cs(1) and Na(1) converged to the same error indices with occupancy of 0.6(2) for Na(2). Considering the small deviation from unity which may be expected for Si/Al (~ 1.04),¹⁶ the unit cell formula of this crystal is taken to be Cs_{2.87}Na_{8.6}H_x-A, x ca. 0.5.⁹ For simplicity, the notation Cs₃Na₉-A will be used. The number of Na⁺ ions may be somewhat greater than 8.6: the 0.13 8-rings per unit cell not occupied by Cs⁺ may contain Na⁺. The final structural parameters are given in Table 1(a). Selected interatomic distances and angles are given in Table 2.

Hydrated Cs₃Na₉-A (crystal 2). Full-matrix least-squares refinement was initiated with the framework atomic parameters [(Si, Al), O(1), O(2), and O(3)] and Cs⁺ at Cs(1) and Na⁺ at Na(1) of the dehydrated Cs₃Na₉-A (crystal 1). The refinement of this initial model converged to the error indices of $R_1=0.173$ and $R_2=0.236$ with anisotropic thermal parameters for all atomic types except for those of isotropi-

cally refined Cs⁺ ions at Cs(1). The resulting model suggested quite different coordination environments around Na⁺ ions at Na(1) and Cs⁺ ions at Cs(1) of 6- and 8-rings, respectively, compared to those of Na⁺ ions in the crystal structures of dehydrated Cs₃Na₈H-A⁶ and Cs₃Na₉-A (crystal 1).

The large values of thermal parameters for Cs⁺ ions at Cs(1) on the 8-rings also suggested a possible off-centering of Cs⁺ ions from the centers of 8-rings. When the point symmetry of Cs⁺ ions at Cs(1) reduced from (0, 1/2, 1/2) to (0.03, 1/2, 1/2) with the anisotropic thermal parameters in this model, least-squares refinement converged with Cs⁺ ions stable at (0.0325, 1/2, 1/2) and with occupancy of 2.63(5) and error indices of 0.114 and 0.167 for R_1 and R_2 , respectively. However, this converged position of Cs⁺ ions at Cs(1) may be due to the unidentified non-framework water molecules around the Cs⁺ ions at this stage of refinement (*vide infra*). The refined position of (0.226, 0.226, 0.226) for Na⁺ ions at Na(1) on the 3-fold axes near the 6-rings suggested

Table 2. Selected Interatomic Distances (Å) and Angles (deg)^a

	(a) Dehydrated Cs ₃ Na ₉ -A (crystal 1)	(b) Hydrated Cs ₃ Na ₉ -A (crystal 2)	(c) Hydrated Cs ₃ Na ₈ H-A (crystal 3)
(Si,Al)-O(1)	1.650(4)	1.659(5)	1.662(9)
(Si,Al)-O(2)	1.651(8)	1.649(8)	1.653(14)
(Si,Al)-O(3)	1.673(4)	1.678(5)	1.681(10)
Na(1)-O(2)	2.938(6)	2.97(2)	2.97(3)
Na(1)-O(3)	2.303(6)	2.35(1)	2.34(2)
Cs(1)-O(1)	3.401(11)	3.392(12)	3.38(2)
Cs(1)-O(2)	3.549(6)	3.591(6)	3.586(10)
Na(2)-O(3)	2.86(10)	—	—
Na(2)-O(1)	2.837(10)	—	—
Na(1)-O(5)	—	2.19(2)	2.35(3)
Na(1)-O(7)	—	2.70(4)	2.73(5)
Cs(1)-O(6)	—	3.26(10)	3.13(11)
O(4)-O(1)	—	3.33(4)	3.47(6)
O(4)-O(2)	—	3.89(4)	3.98(6)
O(4)-O(3)	—	3.06(4)	3.20(5)
O(7)-O(3)	—	3.094(10)	3.172(17)
O(4)-O(5)	—	2.82(5)	2.75(7)
O(5)-O(6)	—	2.55(6)	2.58(7)
O(6)-O(6)	—	3.56(15)	3.25(20)
O(7)-O(7)	—	3.12(9)	2.96(6)
O(1)-(Si,Al)-O(2)	107.1(4)	108.2(5)	107.4(8)
O(1)-(Si,Al)-O(3)	112.1(3)	111.6(4)	111.9(6)
O(2)-(Si,Al)-O(3)	107.6(2)	106.9(2)	107.0(4)
O(3)-(Si,Al)-O(3)	110.1(3)	111.3(4)	111.4(7)
(Si,Al)-O(1)-(Si,Al)	145.9(8)	145.6(8)	144(1)
(Si,Al)-O(2)-(Si,Al)	158.2(5)	160.8(5)	160.4(8)
(Si,Al)-O(3)-(Si,Al)	143.3(4)	143.3(4)	143.4(8)
O(3)-Na(1)-O(3)	118.1(1)	113.6(2)	115.1(3)
Na(1)-O(5)-O(4)	—	105.7(8)	107(1)
O(4)-O(5)-O(4)	—	112.9(8)	112(1)
O(6)-O(5)-O(6)	—	110(2)	111(2)
O(5)-O(6)-O(5)	—	120(4)	114(5)
O(5)-O(6)-O(6)	—	100(2)	102(2)
O(6)-Cs(1)-O(6)	—	66(3)	62(4)
O(5)-Na(1)-O(7)	—	180.0 ^b	180.0 ^b
O(7)-O(7)-O(7)	—	60.0	60.0

^aThe numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding parameters. ^bExactly 180° by symmetry.

tetrahedral geometry around each Na⁺ ion with three framework oxygens at O(3) and a presumable water molecule on the 3-fold axis of the large cavity (*vide infra*).

A series of refinements with water molecule at O(4) introduced from a peak found at (0.27, 0.27, 0.46) in a difference Fourier function were converged with almost 24 oxygens and large isotropic thermal parameter at this position. Since an arrangement with 24 water molecules at this 24-fold position was physically impossible due to too close contacts between some of them, the thermal parameter of oxygens at O(4) was temporarily fixed at 4.0 Å² in subsequent refinement, resulting the occupancy of 7.9(5) oxygens with error indices

of $R_1=0.0908$ and $R_2=0.127$. Other peaks for the non-framework water molecules, O(5) and O(6) at (0.32, 0.32, 0.32) and (0.22, 0.35, 1/2), respectively, from the subsequent difference Fourier functions were also introduced in the same manners in the following refinement. The refinement was converged with $R_1=0.0701$ and $R_2=0.0949$ and resulting occupancies of 2.71(3), 6.1(4), 3.6(2), and 4.2(5) for Cs(1), and O(i), $i=4$ to 6, respectively. When the isotropic thermal parameters of oxygens of O(i), $i=4$ to 6, were varied stepwise together with their occupancies varied fully, the refinement was converged to the error indices of $R_1=0.0649$ and $R_2=0.0874$ with resulting occupancies of 6.5(4), 5.2(3), and 7.0(8) and isotropic thermal parameters of 8.54, 12.9, and 23.9 Å² for O(i), $i=4$ to 6, respectively. In subsequent refinements, occupancies of all oxygens at O(i), $i=4$ to 6, were fixed at 6.0's as the nearest integers, resulting in the error indices of $R_1=0.0656$ and $R_2=0.0881$.

When an additional peak found at (0.11, 0.11, 0.12) in a difference Fourier function was introduced at O(7) in the following refinement, it was converged at a position of (0.094, 0.094, 0.094) on a 3-fold axis with occupancy of 4.3(4) and error indices of $R_1=0.0595$ and $R_2=0.0738$. Finally, when the occupancies of Cs⁺ ions at Cs(1) and of oxygens were fixed at 2.87 (a known value from the crystal structure of dehydrated Cs₃Na₉-A, crystal 1) and at 4.0 and 6.0's for O(7) and O(i), $i=4$ to 6, respectively, the position of Cs⁺ ions at Cs(1) converged to (0, 1/2, 1/2). This final least-squares refinement converged to the error indices of $R_1=0.0626$ and $R_2=0.0734$. The location of 12th Na⁺ ion opposite a 4-ring, found in the dehydrated Cs₃Na₉-A, was not successful due to the large number of water molecules around this position in the large cavity. It is therefore assumed that the twelfth Na⁺ ion is crystallographically not distinguishable from water molecules located around the symmetrically equivalent positions of the common site for this ion. The formula of crystal 2 is however assumed as Cs₃Na₉-A·22H₂O for simplicity. The final structural parameters are given in Table 1(b). Selected interatomic distances and angles are given in Table 2.

Hydrated Cs₃Na₈-A (crystal 3). Full-matrix least-squares refinement began with the atomic parameters of all framework atoms [(Si, Al), O(1), O(2), and O(3)] and Cs⁺ at Cs(1) and Na⁺ at Na(1) in the hydrated Cs₃Na₉-A (crystal 2). The refinement with anisotropic thermal parameters for all atomic types in this model converged to the error indices of $R_1=0.133$ and $R_2=0.178$ with varied occupancies of 2.82(8) for Cs(1). Locations of non-framework water molecules were carried out in the similar manners described for those of hydrated Cs₃Na₉-A. The final cycles of refinement with a fixed occupancy of 2.86 at Cs(1), as proven in the crystal structure of dehydrated Cs₃Na₈H-A,⁶ converged to the error indices of $R_1=0.0768$ and $R_2=0.0787$. As the cases of crystal 2 and dehydrated Cs₃Na₈H-A,⁶ the final formula of crystal 3 is assumed as Cs₃Na₈H-A·22H₂O. The final structural parameters are given in Table 1(c). Selected interatomic distances and angles are given in Table 2.

The values of goodness-of-fit, $(\sum w(F_o - |F_c|)^2 / (m - s))^{1/2}$, are 1.61, 1.88, and 2.39; the number of observations, m , are 254, 251, and 179, and the number of parameters, s , are 29, 37, and 37 for crystals 1 to 3, respectively. All shifts in the final cycles of refinement for both crystals were less than 0.1% of their corresponding estimated standard deviations. The

quantity minimized in the least-squares is $\sum w(F_o - |F_c|)^2$, and the weights (w) are the reciprocal squares of $\sigma(F_o)$, the standard deviation of each observed structure factor. Atomic structure factors for Cs^+ , Na^+ , O^{2-} , O, and (Si, Al)^{1.75+} were used.^{17,18} The function describing (Si, Al)^{1.75+} is the mean of the Si^{4+} , Si^0 , Al^{3+} , and Al^0 functions. All scattering factors were modified to account for anomalous dispersion.^{19,20}

Discussion

Framework and Cations in $\text{Cs}_3\text{Na}_9\text{-A}$ and $\text{Cs}_3\text{Na}_8\text{-H-A}$

A. Atomic parameters of all framework atoms and cations in the crystal structure of dehydrated $\text{Cs}_3\text{Na}_9\text{-A}$ (crystal 1) are almost identical with those in dehydrated $\text{Cs}_3\text{Na}_8\text{-H-A}$,⁶ except for the presence of Na^+ ion at Na(2) located opposite 4-ring in the large cavity. This is probably because of lower concentration of H^+ in the ion-exchange solution for $\text{Cs}_3\text{Na}_9\text{-A}$ (pH=11.7), compared to that for $\text{Cs}_3\text{Na}_8\text{-H-A}$ (pH=5.7).⁶ In all three structures, *ca.* 2.87 Cs^+ ions per unit cell nearly fill the centers of three 8-rings ($\text{Cs}(1)$ at equipoints of local symmetry C_{4h} [D_{4h} in $Pm\bar{3}m$]). Each Cs^+ ion at $\text{Cs}(1)$ of dehydrated $\text{Cs}_3\text{Na}_9\text{-A}$ is 3.401(11) and 3.549(6) Å from four oxygens at O(1) and four oxygens at O(2) of the 8-rings, respectively. In hydrated structures, the corresponding distances are slightly shorter: 3.392(12) and 3.38(2) Å for $\text{Cs}(1)\text{-O}(1)$ and 3.591(6) and 3.586(10) Å for $\text{Cs}(1)\text{-O}(2)$, respectively in crystals 1 and 2 (see Table 2), probably because of relaxed frameworks due to extensive hydration. Although these interatomic distances are substantially longer than the sum of conventional ionic radii of Cs^+ and O^{2-} , $1.67 + 1.32 = 2.99$ Å,²¹ the positions of $\text{Cs}(1)$ are well established by crystal structures of many partially and fully Cs^+ -exchanged zeolites A^{6,22-26} and by theoretical studies.^{27,28} It remains possible that up to $3.0 - 2.87 = 0.13$ Na^+ ions per unit cell are also present to complete the occupation of all 8-rings.

In dehydrated $\text{Cs}_3\text{Na}_9\text{-A}$, the eight Na^+ ions per unit cell at Na(1) have trigonal geometries with three framework oxygens at O(3) with distance of 2.303(6) Å, as indicated by interatomic angle of $118.1(2)^\circ$ for O(3)-Na(1)-O(3) (see Table 2). Similar interatomic distance and angle have been found in the crystal structures of zeolites A without guest molecules of strong ligational properties as shown in those of dehydrated $\text{Na}_{12}\text{-A}$ ²⁹ and $\text{Cs}_3\text{Na}_8\text{-H-A}$.⁶ In the hydrated structures, the corresponding distances are longer and angles are smaller: 2.35(1) and 2.34(2) Å for Na(1)-O(3) and $113.6(2)$ and $115.1(3)^\circ$ for O(3)-Na(1)-O(3) respectively for crystals 2 and 3. These Na^+ ions extend 0.32, 0.61, and 0.53 Å, respectively for crystals 1 to 3, into the large cavity from the (111) plane at O(3) (see Table 3). Therefore, the Na^+ ions at Na(1) have changed their geometries from trigonal to tetrahedral with additional water molecules at the primary coordination spheres of the Na^+ ions in the large cavity upon hydration (*vide infra*).

The presence of twelfth cation as Na^+ at Na(2) for the electric neutrality of negative charge accompanied with framework ($\text{Si}_{12}\text{Al}_{12}\text{O}_{48}$) is expected opposite 4-ring in the large cavity, as found in the crystal structures of many monocation-exchanged zeolite A.²⁹⁻³¹ The occupancy of Na(2) in dehydrated $\text{Cs}_3\text{Na}_9\text{-A}$ turned out to be 0.6(2) and may prove the contrary deviation of Si/Al (=1.04) from unit value.¹⁶ Nonetheless, the relatively lower concentration of H^+

Table 3. Deviations of Atoms (Å) from the (111) Plane at O(3)^a

	(a) Dehydrated $\text{Cs}_3\text{Na}_9\text{-A}$ (crystal 1)	(b) Hydrated $\text{Cs}_3\text{Na}_9\text{-A}$ (crystal 2)	(c) Hydrated $\text{Cs}_3\text{Na}_8\text{-H-A}$ (crystal 3)
Na(1)	0.321	0.605	0.526
O(5)		2.788	2.879
O(7)		-2.096	-2.204

^aA negative deviation indicates that the ion lies on the same side of the plane as the origin, *i.e.*, inside the sodalite unit.

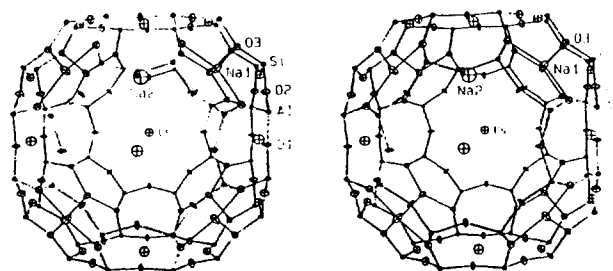


Figure 1. A stereoview of large cavity in dehydrated $\text{Cs}_3\text{Na}_9\text{-A}$. The zeolite A framework is drawn with light bonds between tetrahedrally coordinated (Si,Al) and oxygen atoms. The bonds between the Na^+ ions and framework oxygens are indicated by fine solid lines. Ellipsoids of 20% probability are shown.

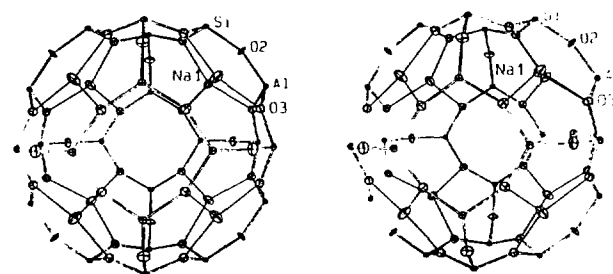


Figure 2. A stereoview of a sodalite unit in dehydrated $\text{Cs}_3\text{Na}_9\text{-A}$. See the caption to Figure 1 for other details.

(pH=11.7) in the ion-exchange solution of $\text{Cs}_3\text{Na}_9\text{-A}$ must have played an important role for having Na^+ ion at Na(2). It is because this Na^+ ion could not be located in dehydrated $\text{Cs}_3\text{Na}_8\text{-H-A}$, ion-exchanged at pH=5.7.⁶ The interatomic distances of 2.84(1) and 2.86(10) Å for Na(2)-O(1) and Na(2)-O(2) (see Table 2), respectively, are rather longer than the normal distance for $\text{Na}^+\text{-O}^{2-}$, probably due to the averaged positions of those oxygens of eleven 4-rings with no Na^+ ions on them. These Na^+ ions at Na(2) in the cases of hydrated crystals were crystallographically undistinguishable from water molecules. The arrangements of framework atoms and cations in the large cavity and sodalite unit of the dehydrated $\text{Cs}_3\text{Na}_9\text{-A}$ are shown in Figures 1 and 2, respectively.

Water Molecules in Hydrated $\text{Cs}_3\text{Na}_9\text{-A}$ and $\text{Cs}_3\text{Na}_8\text{-H-A}$

H-A. The crystal structures of hydrated $\text{Cs}_3\text{Na}_9\text{-A}$ and $\text{Cs}_3\text{Na}_8\text{-H-A}$ revealed a total of 22 water molecules per unit cell, so that their formulars (*vide infra*) were assumed to be $\text{Cs}_3\text{Na}_9\text{-A}$.

Table 4. Distribution of Water Molecules in Hydrated $\text{Cs}_3\text{Na}_9\text{-A}$

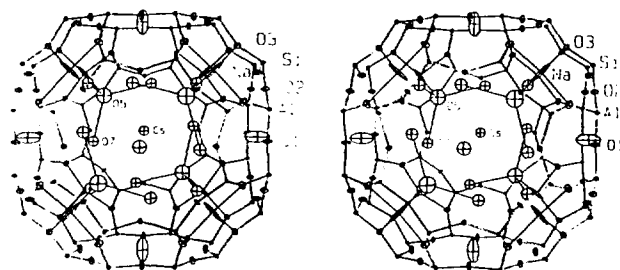
Formular	Number of Water Molecules			
	Sodalite		Large-cavity	
	Components opposite 6-ring	opposite 4-ring	opposite 6-ring	opposite 4-ring
	O(7)	O(5)	O(4) ^a	O(6) ^b
$\text{Cs}_3\text{Na}_9\text{-A} \cdot 22\text{H}_2\text{O}$	4	6	6	6
$\text{Cs}_3\text{Na}_9\text{-A} \cdot 20\text{H}_2\text{O}$	4	4	12	0
$\text{Cs}_3\text{Na}_9\text{-A} \cdot 24\text{H}_2\text{O}$	4	8	0	12

^aOff centered from opposite 4-ring, at Wyckoff position 24(m).^bOff centered from opposite 4-ring, at Wyckoff position 24(l).

$\text{A} \cdot 22\text{H}_2\text{O}$ and $\text{Cs}_3\text{Na}_8\text{H-A} \cdot 22\text{H}_2\text{O}$ for crystals 2 and 3, respectively. The most prominent differences for the atomic parameters of framework atoms and cations in the crystal structures of hydrated $\text{Cs}_3\text{Na}_9\text{-A}$ (crystal 2) and $\text{Cs}_3\text{Na}_8\text{H-A}$ (crystal 3) from those of dehydrated $\text{Cs}_3\text{Na}_9\text{-A}$ (crystal 1) and $\text{Cs}_3\text{Na}_8\text{H-A}^6$ are found in the coordination environments of Cs^+ and Na^+ ions on the 8- and 6-rings, respectively, due to the approaches of additional water molecules to the primary coordination spheres of the cations. The temporarily converged position of (0.0325, 1/2, 1/2) for the Cs^+ ions at Cs(1) in the early stage of least-squares refinement (*vide supra*) was the indication of these approaches by water molecules at O(4) and O(6) and this position is within a displacement value of the final position, center of the 8-ring (see Table 1). Tetrahedron geometry around each Na^+ ion at Na(1) is obvious with three framework oxide anions at O(3) and additional water molecule at O(5) on a 3-fold axis in the large cavity.

However, the presence of inevitable close contacts between water molecules at O(4) and O(6) in the large cavity suggested disordered characters of secondary structures of those zeolitic water molecules. Therefore, the crystal structures of hydrated ones are viewed as having two component cells of $\text{Cs}_3\text{Na}_9\text{-A} \cdot x\text{H}_2\text{O}$ and $\text{Cs}_3\text{Na}_9\text{-A} \cdot y\text{H}_2\text{O}$ (component cells 1 and 2, respectively), where $x=0$ and 1 for crystals 2 and 3, respectively. See Table 4 for the composition and distribution of water molecules in each component cell.

In the crystal structure of $\text{Cs}_3\text{Na}_9\text{-A} \cdot 20\text{H}_2\text{O}$ (component cell 1), twenty water molecules are distributed among three crystallographically distinct positions: twelve off-centered opposite 4-rings at O(4) in large cavity, four on the 3-fold axes at O(5) in the large cavity, and finally four on 3-fold axes at O(7) in sodalite unit, respectively. In each large cavity of $\text{Cs}_3\text{Na}_9\text{-A} \cdot 20\text{H}_2\text{O}$, four water molecules at O(5) are directly coordinated to four Na^+ ions of the 6-rings at Na(1). This change in geometry around Na^+ ions at Na(1) from trigonal to tetrahedron can also be seen at the changes of interatomic angles, from 118.1(2) to 113.4(2) for O(3)-Na(1)-O(3) upon dehydration of hydrated $\text{Cs}_3\text{Na}_9\text{-A}$ (see Table 2). The interatomic distances of 2.18(3) Å between Na^+ ions at Na(1) and oxygens at O(5) are rather shorter than the sum, 2.31 Å, of ionic radii of Na^+ and O^{2-} , probably because the distances are averaged ones with Na^+ ions located on the 6-rings with

**Figure 3.** A stereoview of large cavity in $\text{Cs}_3\text{Na}_9\text{-A} \cdot 20\text{H}_2\text{O}$. See the caption to Figure 1 for other details.

different coordination environments as suggested by the large elongated values of their thermal parameters (see Table 1). Efforts for the deconvolution of different kinds of Na^+ ions at Na(1), however, were unsuccessful. Three additional oxygens at O(4) from off-centered opposite 4-rings of adjacent octants in the large cavity are in turn coordinated to each oxygen at O(5), showing tetrahedron geometry around the oxygen atom of the water molecule at O(5) with angles of 113.0(8) and 105.7(9)° for O(4)-O(5)-O(4) and Na(1)-O(5)-O(4), respectively. The interatomic distances between oxygens at O(4) and O(5) are 2.83(6) Å, indicating the formation of hydrogen bonds between them. The water molecules at O(4) are 3.33(4) and 3.88(5) Å away from framework oxide anions of O(1) and O(2), respectively, far enough to be considered as having no direct interactions between them except for those with O(3) at 3.05(4) Å. The four water molecules at O(5), each with three water molecules at O(4) in its primary coordination sphere, are arranged tetrahedrally in the large cavity as shown in Figure 3.

In the large cavity of $\text{Cs}_3\text{Na}_9\text{-A} \cdot 24\text{H}_2\text{O}$ (component cell 2), two distinct positions were identified for non-framework water molecules at O(5) and O(6), opposite 6-rings on 3-fold axes and off-centered opposite 4-rings, respectively. Twelve water molecules at O(6) and eight at O(5) per unit cell seem to construct a pseudo-dodecahedron, suggested in the crystal structure of hydrated $\text{Na}_{12}\text{-A}$.² Each pentagon of the pseudo-dodecahedron is consisted of three water molecules at O(6), two from the same plane and one from adjacent plane of a virtual cube drawn with eight oxygens of O(5) at its corners, and two at O(5) as -O(6)-O(5)-O(6)-O(5)-O(6)-. Each water molecule at O(5) in turn coordinated to the 6-ring Na^+ ion at Na(1), having tetrahedron geometry around it with three oxygen atoms at O(6), as similarly described in component cell 1. The interatomic distances between oxygen atoms of each pentagon at O(5) and O(6) are 2.51(6) Å with angles of 109(3) and 117(3)° for O(6)-O(5)-O(6) and O(5)-O(6)-O(5), respectively. The only perturbation from the ideal pentagon occurs in the position of the two water molecules at O(6) on the same plane. The interatomic distance, 3.59(16) Å, between the two oxygen atoms at O(6) got longer than the other bonds of the pentagon, because of the close approach of Cs^+ ion to these water molecules with distances of 3.34(10) Å. This is indicative with the large values of thermal parameters for both O(6) and Cs(1) (see Table 1). The arrangement of twenty water molecules, eight and twelve water molecules at O(5) and O(6), respectively, in the large cavity of $\text{Cs}_3\text{Na}_9\text{-A} \cdot 24\text{H}_2\text{O}$ are shown in Figure 4. The cluster of twenty water molecules with Cs^+ ions and presumed do-

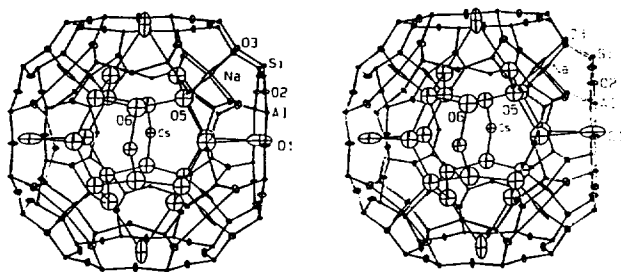


Figure 4. A stereoview of large cavity in $\text{Cs}_3\text{Na}_9\text{-A}\cdot 24\text{H}_2\text{O}$. See the caption to Figure 1 for other details.

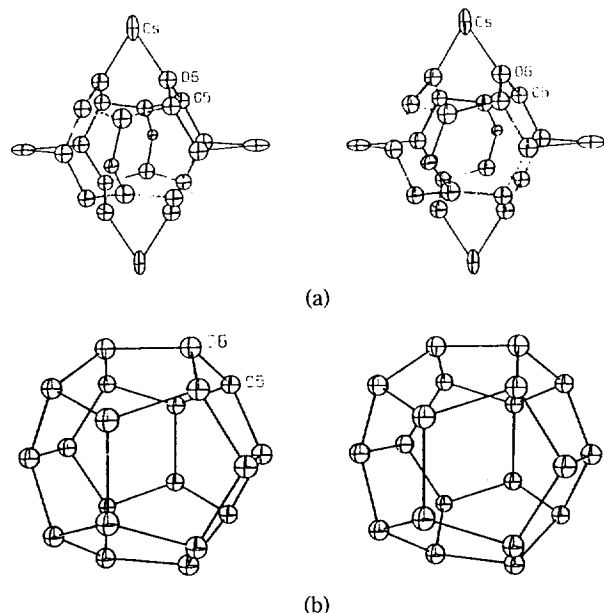


Figure 5. (a) A stereoview of pseudo-dodecahedron of zeolitic water molecules in large cavity of $\text{Cs}_3\text{Na}_9\text{-A}\cdot 24\text{H}_2\text{O}$, showing close approaches of Cs^+ to water molecules at O(6). (b) A stereoview of presumed dodecahedron with a slight modification in the position of O(6) with no perturbation of Cs^+ ions. See the caption to Figure 1 for other details.

dodecahedron with a slight modification in the position of O(6), assuming no perturbation raised by the Cs^+ ions at Cs(1), are shown in Figure 5.

In the sodalite units of both component cells of $\text{Cs}_3\text{Na}_9\text{-A}\cdot 22\text{H}_2\text{O}$, four water molecules at O(7) are located tetrahedrally in four symmetry equivalent positions on 3-fold axes. The averaged interatomic distance between oxygens at O(7) and Na^+ ions at Na(1) is 2.64(4) Å, which is substantially longer than the value, 2.31 Å found for the normal approach of oxygens to the Na^+ ion. This is partly because six Na^+ ions among eight of total Na^+ ions per unit cell participate in forming tetrahedral geometries with water molecules at O(5) from the large cavity (*vide supra*). Therefore, in the averaged structure of sodalite units, no particular direct interactions between water molecules at O(7) and Na^+ ions at Na(1) are expected. These water molecules seem to have interactions with framework oxide anions and themselves in terms of hydrogen bondings. The interatomic distances are 3.04(10) and 3.25(10) Å for O(7)-O(3) and O(7)-O(7), res-

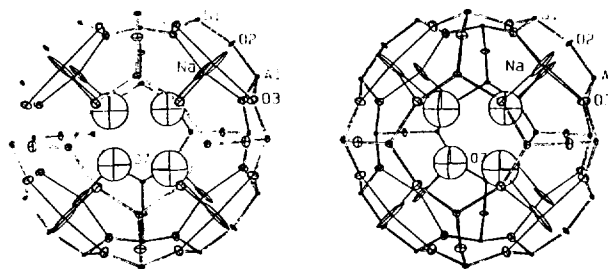


Figure 6. A stereoview of a sodalite unit in hydrated $\text{Cs}_3\text{Na}_9\text{-A}\cdot 22\text{H}_2\text{O}$. See the caption to Figure 1 for other details.

pectively (see Table 2). The tetrahedral arrangement of the water molecules at O(7) in the sodalite units is shown in Figure 6.

Structures of zeolitic water molecules in the hydrated $\text{Cs}_3\text{Na}_8\text{H-A}$ (crystal 3) are expected to be similar to those described above, except for slight difference raised by the absence of the 12th Na^+ ion in the large cavity. The arrangements of zeolitic water molecules, found in the crystal structure of hydrated $\text{Cs}_3\text{Na}_9\text{-A}$ (crystal 2), are examined and confirmed. However, no further detailed work for the structure of hydrated $\text{Cs}_3\text{Na}_8\text{H-A}$ was carried out due to smaller numbers of diffraction intensities for this crystal.

Acknowledgement. We gratefully acknowledge the support of the Central Laboratory of Kyungpook National University for the purchase of the diffractometer and computing facilities.

Supplementary Material Available. Observed and calculated structure factors for fully dehydrated $\text{Cs}_3\text{Na}_9\text{-A}$, hydrated $\text{Cs}_3\text{Na}_9\text{-A}$, and hydrated $\text{Cs}_3\text{Na}_8\text{H-A}$. Ordering information is given on any current masthead page.

References

- Teeter, M. M. *Proc. Natl. Acad. Sci. USA* **1984**, *81*, 6014.
- Gramlich, V.; Meier, W. M. *Z. Kristallogr.* **1971**, *133*, 134.
- Water, A. *Comprehensive Treatise*; Franks, F. Ed.; Plenum Press: New York, 1972; 104-107 and references therein.
- Yoon, B. J.; Jhon, M. S. *Bull. Korean Chem. Soc.* **1991**, *12*, 67 and references therein.
- McCusker, L. B.; Baerlocher, Ch.; Jahn, E.; Bulow, M. *Zeolites* **1991**, *11*, 308.
- Heo, N. H.; Cho, K. H.; Seff, K. *J. Am. Chem. Soc.* submitted for publication.
- Heo, N. H.; Yoon, J. H. *J. Phys. Chem.* **1992**, *96*, 4997.
- Heo, N. H.; Kwon, J. H.; Cho, K. H.; Kim, H. W.; Suh, S. H. *Bull. Korean Chem. Soc.* **1993**, *14*, 583.
- The nomenclature refers to the content of the $Pm\bar{3}m$ unit cell, $\text{Na}_{12}\text{-A}$. $\text{Cs}_3\text{Na}_9\text{-A}$ and $\text{Cs}_3\text{Na}_8\text{H-A}$ represent $\text{Cs}_3\text{Na}_9\text{Si}_{12}\text{Al}_{12}\text{O}_{48}$ and $\text{Cs}_3\text{Na}_8\text{HSi}_{12}\text{Al}_{12}\text{O}_{48}$, respectively.
- Charnell, J. F. *Crystal Growth* **1971**, *8*, 291.
- Heo, N. H.; Rho, B. R.; Kim, D. H.; Kim, J. T. *Hwahak Konghak* **1991**, *29*, 407.
- Cruz, W. V.; Leung, P. C. W.; Seff, K. *J. Am. Chem. Soc.* **1978**, *100*, 6997.
- Mellum, M. D.; Seff, K. *J. Phys. Chem.* **1984**, *88*, 3560.
- Calculation were performed with *Structure Determination System, MolEN*; Enraf-Nonius: Netherlands, 1990.

15. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, **1974**, 4, p 61-66.
16. Blackwell, C. S.; Pluth, J. J.; Smith, J. V. *J. Phys. Chem.* **1985**, 89, 4420.
17. Doyle, P. A.; Turner, P. S. *Acta Crystallogr. Sect. A* **1968**, 24, 390.
18. Reference 15, p 73-87.
19. Cromer, D. T. *Acta. Crystallogr.* **1965**, 18, 17.
20. Reference 15, p 149-150.
21. *Handbook of Chemistry and Physics*; Chemical Rubber Co., Cleveland, OH 64th ed.; 1983; p F-187.
22. Heo, N. H.; Seff, K. *J. Am. Chem. Soc.* **1987**, 109, 7986.
23. Heo, N. H.; Seff, K. *Zeolites* **1992**, 12, 819.
24. Vance, Jr. T. B.; Seff, K. *J. Phys. Chem.* **1975**, 79, 2163.
25. Firor, R. L.; Seff, K. *J. Am. Chem. Soc.* **1977**, 99, 6249.
26. Subramanian, V.; Seff, K. *J. Phys. Chem.* **1979**, 83, 2166.
27. Ogawa, K.; Nitta, M.; Aomura, K. *J. Phys. Chem.* **1979**, 82, 1665.
28. Takaishi, T.; Hosoi, H. *J. Phys. Chem.* **1982**, 86, 2089.
29. Yanagida, R. Y.; Amaro, A. A.; Seff, K. *J. Phys. Chem.* **1973**, 77, 805.
30. Leung, P. C. W.; Kunz, K. B.; Maxwell, I. E.; Seff, K. *J. Phys. Chem.* **1975**, 79, 2157.
31. Kim, Y.; Seff, K. *J. Phys. Chem.* **1978**, 82, 1071.

Use of a Cationic Hydrido-aquo-palladium(II) Complex As a Catalyst for Olefin Hydroesterification

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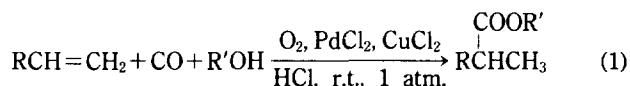
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Received December 10, 1993

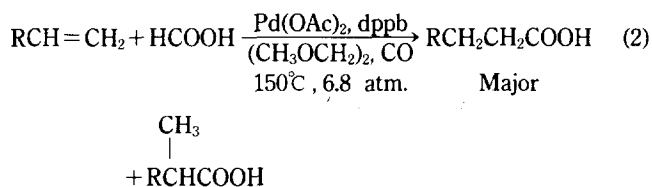
The cationic palladium complex, $(\text{Cy}_3\text{P})_2\text{Pd}(\text{H})(\text{H}_2\text{O})^+\text{BF}_4^-$, **1**, catalyzes the hydroesterification of olefins to give straight-chain esters as the major products. The catalytic system consists of **1**, *p*-toluenesulfonic acid, 1,4-bis(diphenylphosphino)butane.

Introduction

A reaction which has been the subject of many publications and patents is the metal complex catalyzed hydroesterification and hydrocarboxylation of olefins.^{1,2} Most of the research in this area has utilized palladium compounds as catalysts. For example, branched chain esters or acids are obtained in good yields when palladium chloride catalyzes the reaction of an olefin with carbon monoxide and an alcohol or water in the presence of copper(II) chloride, hydrochloric acid, and oxygen Eq. (1).³ Another approach utilizes formic



acid with palladium acetate and 1,4-bis(diphenylphosphino)butane [dppb] as the catalytic system for the regioselective synthesis of straight chain acids from olefins⁴ Eq. (2) and for the



conversion of alkynes to unsaturated acids.⁵

Recently, the cationic hydrido-aquo-palladium(II) complex, *trans*- $[(\text{Cy}_3\text{P})_2\text{Pd}(\text{H})(\text{H}_2\text{O})]^+\text{BF}_4^-$ **1** was described in the literature.⁶ The novel palladium complex has, in addition to bulky tricyclohexylphosphine ligands, hydrido and aquo ligands attached to the metal. It was of interest to assess the catalytic activity and regioselectivity of **1** for the hydroesterification reaction. The cationic palladium(II) diphosphine complexes, $[(\text{dppp})\text{Pd}(\text{solvent})_2][\text{X}]_2$, where X is a non or weakly coordinating anion, have been used for the carbonylation of olefins to ketones.⁷ We now report the regioselective hydroesterification of olefins to straight chain esters, catalyzed by **1** under appropriate conditions.

Results and Discussion

No reaction occurred when styrene was treated with carbon monoxide and methanol in tetrahydrofuran (THF) at 20.4 atmospheres and 100°C for 48 hours, using **1** as the catalyst [77/1.0 ratio of styrene: **1**]. Recently, Drent⁸ showed that *p*-toluenesulfonic acid (*p*-TsOH) is an important component for the palladium catalyzed copolymerization of ethylene and carbon monoxide. When the reaction of styrene [**2**, R = Ph] was repeated in the presence of *p*-TsOH [2:1 ratio of *p*-TsOH/1], methyl 3-phenylpropionate [**3**, R = Ph] was formed in 26% yield and methyl 2-phenylpropionate [**4**, R = Ph] was isolated in 30% yield. Inferior results were obtain-