

# Hydronium Ions in Zeolites. 1. Structures of Partially and Fully Dehydrated Na,H<sub>3</sub>O–X by X-ray and Neutron Diffraction

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The crystal chemistry of hydronium ions in zeolite X has been investigated by single-crystal X-ray and powder neutron diffraction. By titration of Na<sub>96</sub>Si<sub>96</sub>Al<sub>96</sub>O<sub>384</sub> with HCl, a break in the pH was observed at 6.35, at about 33 H<sub>3</sub>O<sup>+</sup> ions per unit cell. The structure of zeolite X in equilibrium with 0.1 M aqueous Na<sup>+</sup> at pH 6.35 was determined by single-crystal X-ray diffraction techniques in the cubic space group *Fd* $\bar{3}$  at 20 °C after partial dehydration (Na<sub>60</sub>(H<sub>3</sub>O)<sub>32</sub>(H<sub>2</sub>O)<sub>24</sub>Si<sub>100</sub>Al<sub>92</sub>O<sub>384</sub>, *a* = 25.128(4) Å) and in *Fd* $\bar{3}m$  after complete dehydration (Na<sub>60</sub>H<sub>32</sub>Si<sub>100</sub>Al<sub>92</sub>O<sub>384</sub>, *a* = 25.101(2) Å). In the partially dehydrated crystal, Na<sup>+</sup> ions are found at three different crystallographic sites and H<sub>3</sub>O<sup>+</sup> ions are found at two. Two different site I' positions are occupied by 16 Na<sup>+</sup> and 16 H<sub>3</sub>O<sup>+</sup> ions, respectively, per unit cell; a water molecule bridges between two of each in each sodalite cage to give eight near tetrahedral (H<sub>3</sub>O<sup>+</sup>)<sub>2</sub>H<sub>2</sub>O(Na<sup>+</sup>)<sub>2</sub> clusters. Two different site III' positions in the supercage are occupied by 16 Na<sup>+</sup> and 16 H<sub>3</sub>O<sup>+</sup> ions, respectively; a water molecule bridges between one of each to give 16 (H<sub>3</sub>O<sup>+</sup>)(H<sub>2</sub>O)(Na<sup>+</sup>) clusters. Thus a structural basis for the great selectivity of zeolite Na–X for H<sub>3</sub>O<sup>+</sup> at near neutral pHs is demonstrated. The remaining 28 Na<sup>+</sup> ions are at site II. In the fully dehydrated single crystal, the 60 Na<sup>+</sup> ions are found at four crystallographic sites. Approximately 6 and 20 Na<sup>+</sup> ions per unit cell at sites I and I', respectively, effectively fill the double six-rings. Thirty-two Na<sup>+</sup> ions fill site II and the remaining two are at site III'. To avoid Na<sup>+</sup> ions, at least 20 of the 32 H<sup>+</sup> ions per unit cell should be in the supercage. Finally, neutron diffraction of Na<sub>54</sub>(D<sub>3</sub>O)<sub>42</sub>Si<sub>96</sub>Al<sub>96</sub>O<sub>384</sub> • 80D<sub>2</sub>O at 10 K revealed the structures of the 16 D<sub>3</sub>O<sup>+</sup> ions in the sodalite units: D–O = 1.13(1) Å and D–O–D = 88(1)°. Each deuteron hydrogen bonds to a framework oxygen atom at 1.53(1) Å. The O···O hydrogen-bonding distance is 2.63(1) Å and the O–D···O angle is 161°.

## Introduction

Some of the exchangeable cations in zeolites are readily replaced by hydronium ions upon contact with water. For example, the pH of distilled water increases to about 10 or 10.5 when fully Na<sup>+</sup>-exchanged zeolite A is slurried into it.<sup>1</sup> Zeolite A Ca<sup>2+</sup>-exchanged from near neutral solution and dehydrated is a Brønsted acid catalyst, presumably because not only Ca<sup>2+</sup> but also H<sub>3</sub>O<sup>+</sup> ions entered the zeolite during ion-exchange; Ca<sup>2+</sup> ions hydrolyze only slightly in aqueous solution.<sup>2</sup> Cook et al. studied the relative H<sub>3</sub>O<sup>+</sup>/Na<sup>+</sup> affinity of the six-ring exchange sites of Na–A.<sup>3</sup> At pH 6.5 ([H<sub>3</sub>O<sup>+</sup>] = 3 × 10<sup>−7</sup> M), half of these exchange sites are occupied by H<sub>3</sub>O<sup>+</sup> ions when [Na<sup>+</sup>] in solution is 5 × 10<sup>−3</sup> M. This shows that zeolite A is very selective for H<sub>3</sub>O<sup>+</sup> at near neutral pHs. As the pH decreases, the extent of H<sub>3</sub>O<sup>+</sup> exchange increases. Townsend et al. studied H<sub>3</sub>O<sup>+</sup> exchange into zeolites X and Y as a function of the pH<sup>4</sup> and the Na<sup>+</sup> concentration of the exchange solutions.<sup>5</sup>

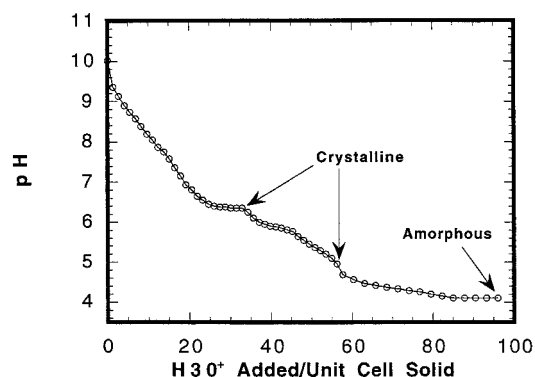
When these zeolites in their sodium forms were added to NaNO<sub>3</sub> solutions, the observed sharp increase in pH was attributed to partial H<sub>3</sub>O<sup>+</sup> exchange. This behavior is qualitatively similar to that observed by Drummond et al. for Na–A in water.<sup>6</sup> Townsend et al. found extensive exchange of H<sub>3</sub>O<sup>+</sup> into zeolites X and Y (up to 17% for zeolite X) and concluded that it is an intrinsic part of the ammonium exchange process, a common first step in the preparation of zeolite acid catalysts. They also found that the extent of H<sub>3</sub>O<sup>+</sup> exchange depends on the Si/Al ratio of the zeolite.<sup>7</sup>

The structure of dehydrated Na–X of composition Na<sub>88</sub>Si<sub>104</sub>–Al<sub>88</sub>O<sub>384</sub> was determined at room temperature by Olson by single-crystal X-ray crystallography with a unusually large data set.<sup>8</sup> Sodium ions were found at seven different crystallographic sites. Cheetham et al. studied Na–X (Si/Al = 1.2) by powder methods at 5 K and found Na<sup>+</sup> ions at only three crystallographic sites;<sup>9</sup> they supported their results with simulations of cation positioning by Monte Carlo techniques. Recent single-crystal work at 21 °C by Zhu and Seff,<sup>10</sup> using a crystal from the same batch<sup>11</sup> and with the same framework composition as the single crystals used in this work, finds Cheetham's three positions<sup>9</sup> and a fourth at a second III' site.

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**Figure 1.** Titration curve of Na-X with 0.1 N HCl. Breaks in the curve are observed at about 33 and 56  $\text{H}_3\text{O}^+$  ions added per unit cell of zeolite.

Preliminary  $\text{NH}_4^+$  and  $\text{H}_3\text{O}^+$  ion-exchange experiments with Na-X type zeolites indicated retention of crystallinity at relatively high  $\text{H}_3\text{O}^+$  exchange levels. Ultimately, however, as  $\text{H}_3\text{O}^+$  exchange proceeds further, zeolite X, like other high-alumina aluminosilicate zeolites, decomposes. Fully  $\text{H}_3\text{O}^+$ -exchanged zeolite X has lost its crystallinity entirely. Kühl et al. studied the crystallinities of dehydrated and deaminated Na,H-X samples obtained by calcination of  $\text{Na}_9\text{NH}_4\text{-X}$ . Their results suggest that zeolite X of initial composition  $\text{Na}_{92}\text{Si}_{100}\text{-Al}_{92}\text{O}_{384}$  would survive calcination if not more than 32  $\text{H}^+$  ions are generated per unit cell.<sup>11</sup>

This work was done to determine the siting and structure of  $\text{H}_3\text{O}^+$  ions in zeolite X, to learn something about the stability of hydronium ions in zeolite X and of zeolite X in the presence of hydronium ions, as a function of temperature, and, after complete dehydration, to learn something about the positions of the resulting  $\text{H}^+$  ions.

## Experimental Section

**(1) Acid Titration of Zeolite X.** Acid titrations/exchanges were conducted to lay the groundwork for the preparation of materials for the structural studies. They were conducted at 25 °C with 0.1 N HCl. Typically, sequential acid additions were at 1 min intervals. Following the titration, the slurry was washed lightly on a filter with deionized water and dried under ambient conditions.

The titration curve of Na-X (LSX, Si/Al = 1) with 0.1 N HCl is shown in Figure 1. Following an initial monotonic decline in pH with acid addition, breaks in the curve are observed at about 33 and 56  $\text{H}_3\text{O}^+$  ions added per unit cell of zeolite. Separate experiments show that the product zeolite remains highly crystalline at these points. At 96  $\text{H}_3\text{O}^+$  ions added per unit cell (1.0  $\text{H}_3\text{O}^+$  added per  $\text{Na}^+$ ) the product solid is amorphous. The structural studies were performed to determine the structural basis for the first break in the titration curve, namely, the site distributions of the sodium and hydronium ions. This occurs at pH ca. 6.35.

**(2) Sample Preparation.** (a) *Single Crystals.* Large single crystals of sodium zeolite X of stoichiometry  $\text{Na}_{92}\text{Si}_{100}\text{Al}_{92}\text{O}_{384}$  were prepared in St. Petersburg, Russia.<sup>12</sup> Two of these, colorless octahedra about 0.15 mm in cross-section, were lodged in fine Pyrex capillaries. Equilibrium was achieved by allowing 0.1 M aqueous  $\text{CH}_3\text{COONa}$  solution (pH adjusted from 8.10 to 6.35 by adding  $\text{CH}_3\text{COOH}$ ) to flow past the crystal at a velocity of approximately 10 mm/s for 48 h at 20(1) °C. The first crystal (crystal 1) was then dehydrated at  $1 \times 10^{-5}$  Torr for 48 h; this was done at 20(1) °C so that any  $\text{H}_3\text{O}^+$  that might be present would not decompose. The resulting crystal, under vacuum in

its capillary, was sealed and removed from the vacuum line by torch. The second crystal (crystal 2) was dehydrated at 150 °C and  $1 \times 10^{-5}$  Torr for 48 h. It was then sealed in its capillary by torch. Both crystals remained colorless.

(b) *Powder Sample.* A high quality sample of Na-LSX with no observable impurities was obtained. It was titrated with 0.1 N HCl to a pH of 5.8. The acid added is equivalent to 45  $\text{H}_3\text{O}^+$  ions per unit cell. Sodium analysis gave 10.0 wt % Na which corresponds to 53.5  $\text{Na}^+$  and 42.5  $\text{H}_3\text{O}^+$  ions per unit cell, indicating essentially quantitative replacement of each lost  $\text{Na}^+$  by  $\text{H}_3\text{O}^+$ . The material was deuterated by 10 cycles of (a) partial dehydration by vacuum heating for 30 min at 45 °C and (b) saturation at 25 °C with  $\text{D}_2\text{O}$  in excess of the amount needed to completely rehydrate the zeolite. After the last deuteration cycle the material was dehydrated for 16 h at 25 °C down to a pressure of about 1 Torr.

**(3) Crystallographic.** (a) *Single Crystals.* The reflection conditions (*hkl*:  $h + k, k + l, l + h = 2n$ , *okl*:  $k + l = 4n$ ) indicate that the space group is either  $Fd\bar{3}$  or  $Fd\bar{3}m$ . The cubic space group  $Fd\bar{3}$  was used for crystal 1. This choice is supported (a) by the low Si/Al ratio, that in turn requires, at least in the short range, alternation of Si and Al according to Loewenstein's rule;<sup>13</sup> (b) by the diffraction intensity data that showed strong intensity inequalities for some *hkl* and *khl* reflection pairs, indicating the absence of the mirror plane of  $Fd\bar{3}m$ ;<sup>14</sup> and (c) by the diffraction data themselves that refined to error indexes lower in  $Fd\bar{3}$  than in  $Fd\bar{3}m$ , with mean Al-O distances ca. 0.06 Å longer than mean Si-O distances.<sup>14</sup>

For crystal 2, however,  $Fd\bar{3}$  was rejected and the space group  $Fd\bar{3}m$  was used. In least-squares refinement only an insignificant difference (ca. 0.01 Å) was seen between the mean Al-O and Si-O distances, and no increases in error indexes were seen when the space group was changed to  $Fd\bar{3}m$ . The erasure of the difference between Al-O and Si-O distances indicates that the Si,Al composition at the Si position is essentially the same as that at the Al position, and therefore the same as that of the entire crystal: the long-range Si,Al ordering has been lost. This can occur most easily if antodomains have formed.<sup>15</sup>

Diffraction data were collected at 20(1) °C with an automated Siemens P3 four-circle computer-controlled diffractometer equipped with a pulse-height analyzer and a graphite monochromator. Molybdenum radiation ( $\text{K}\alpha_1$ ,  $\lambda = 0.70930$  Å;  $\text{K}\alpha_2$ ,  $\lambda = 0.71359$  Å) was used. The unit-cell constants for both crystals were determined by least-squares refinement of 30 intense reflections for which  $14^\circ < 2\theta < 28^\circ$ . The  $\theta$ - $2\theta$  scan technique was used for data collection. Each reflection for which  $4^\circ < 2\theta < 50^\circ$  was scanned at a constant rate of  $3.0^\circ \text{ min}^{-1}$  in  $\omega$  from  $1.0^\circ$  below the  $\text{K}\alpha_1$  peak to  $1.0^\circ$  above the  $\text{K}\alpha_2$  maximum. Background intensity was counted at each end of a scan range for a time equal to one-half the scan time. The intensities of three reflections in diverse regions of reciprocal space were recorded every 97 reflections to monitor crystal and instrument stability. Only small random fluctuations of these check reflections were observed.

Standard deviations were assigned to individual reflections by  $\sigma(I) = [\omega^2(\text{CT} + B_1 + B_2) + (pI)^2]^{1/2}$  where CT is the total integrated count,  $B_1$  and  $B_2$  are the background counts, and  $I$  is the intensity. The values of  $p$  for the two crystals converged to 0.0027 and 0.0010, respectively, in the final refinement of the structure. Lorentz, polarization, and profile corrections were made to the intensities; the contribution of the monochromator crystal was calculated assuming it to be half-perfect and half-mosaic in character. Because the crystals were regular octahedra with no heavy atoms, it was decided that an absorption

TABLE 1: Positional,<sup>a</sup> Thermal,<sup>b</sup> and Occupancy Parameters

atom	Wyc. position	cation site	x	y	z	$U_{11}^c$ or $U_{iso}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$	occupancy <sup>d</sup>	
												varied	fixed
(a) Crystal 1, Na <sub>60</sub> (H <sub>3</sub> O) <sub>32</sub> (H <sub>2</sub> O) <sub>24</sub> Si <sub>100</sub> Al <sub>92</sub> O <sub>384</sub>													
Si	96(g)		−537(1)	1258(1)	355(1)	17(2)	16(1)	14(1)	1(1)	0(1)	−2(1)		96
Al	96(g)		−544(1)	363(1)	1250(1)	14(1)	12(1)	13(1)	0(1)	1(1)	−4(1)		96
O(1)	96(g)		−1075(4)	−1(2)	1051(2)	28(3)	27(3)	26(3)	−6(3)	2(3)	−8(3)		96
O(2)	96(g)		−10(2)	−23(2)	1430(2)	24(3)	20(3)	25(3)	8(2)	4(3)	−6(2)		96
O(3)	96(g)		−327(2)	772(2)	749(2)	24(3)	22(2)	20(3)	3(3)	2(2)	2(2)		96
O(4)	96(g)		−714(2)	711(2)	1809(2)	25(3)	22(3)	26(3)	−2(3)	5(3)	−11(3)		96
Na(I′)	32(e)	I′	547(3)	547(3)	547(3)	31(4)						17.0(15)	16
O(I′)	32(e)	I′	676(5)	676(5)	676(5)	20(5)						15.6(24)	16
O(5)	48(f)		1250	1250	1520(19)	138(43) <sup>e</sup>	138(43) <sup>e</sup>	16(12)	105(39)	0	0	8.6(22)	8
Na(II)	32(e)	II	2330(2)	2330(2)	2330(2)	35(3)	35(3)	35(3)	19(2)	19(2)	19(2)	30.5(6)	
O(III′)	96(g)	III′	1920(17)	2363(18)	4166(14)	75(14)						15.5(21)	16
Na(III′)	96(g)	III′	1757(20)	1850(22)	4179(15)	184(21)						15.9(22)	16
O(6)	96(g)		917(25)	1427(29)	4485(31)	143(27)						12.8(18)	16
(b) Crystal 2, Na <sub>60</sub> H <sub>32</sub> Si <sub>100</sub> Al <sub>92</sub> O <sub>384</sub>													
Si	192(i)		−544(2)	1248(2)	355(1)	21(2)	15(2)	17(2)	−3(2)	2(2)	−2(2)		192
O(1)	96(g)		−1085(3)	1085(3)	0(4)	30(5)	30(5)	32(7)	8(5)	5(4)	5(4)		96
O(2)	96(g)		−32(3)	−32(3)	1418(4)	22(4)	22(4)	28(7)	9(5)	8(4)	8(4)		96
O(3)	96(g)		−711(4)	−711(4)	353(5)	52(6)	52(6)	28(8)	13(7)	11(5)	11(5)		96
O(4)	96(g)		1778(4)	1778(4)	3174(5)	36(5)	36(5)	34(7)	19(6)	−5(5)	−5(5)		96
Na(I)	16(c)	I	0	0	0	45(22)	45(22)	45(22)	30(23)	30(23)	30(23)	5.8(5)	6
Na(I′)	32(e)	I′	477(6)	477(6)	477(6)	47(8)	47(8)	47(8)	16(7)	16(7)	16(7)	20.5(10)	20
Na(II)	32(e)	II	2301(4)	2301(4)	2301(4)	45(4)	45(4)	45(4)	20(5)	20(5)	20(5)	34.6(27)	32
Na(III′)	96(g)	III′	638(16)	638(16)	4170(24)	30 <sup>f</sup>							2

<sup>a</sup> Positional parameters are given  $\times 10^4$ . <sup>b</sup> Thermal parameters have the units  $\text{\AA}^2 \times 10^3$ . Numbers in parentheses are the esd's in the units of the least significant digit given for the corresponding parameter. <sup>c</sup> The anisotropic temperature factor =  $\exp[(-2\pi^2 a^{-2})(h^2 U_{11} + k^2 U_{22} + l^2 U_{33} + 2hkU_{12} + 2hlU_{13} + 2klU_{23})]$ . <sup>d</sup> Occupancy factors are given as the number of atoms or ions per unit cell. <sup>e</sup>  $U_{11}$  and  $U_{22}$  were constrained to be equal. <sup>f</sup> These  $U_{iso}$  values were held fixed in refinement.

correction was unnecessary. Of the 3473 and 3761 reflections gathered for crystals 1 and 2, respectively, 1180 and 716 of which were independent (merging  $R = 0.038$  and  $0.095$ ), only the 374 and 183 reflections, respectively, for which the net count exceeded 3 times its standard deviation were used in subsequent structure determination.

(b) *Powder Sample.* Time-of-flight (TOF) pulsed-neutron diffraction profiles were recorded at 10 K using the high-intensity powder diffractometer (HIPD) at the Manuel Lujan, Jr. Neutron Scattering Center (LANSCE) at Los Alamos National Laboratory. The exposure time for the sample contained in a  $3/8 \times 2$  in.<sup>2</sup> vanadium can was 6.58 h with the neutron source operating at 70  $\mu\text{A}$ . Data from detectors positioned at  $+153^\circ$ ,  $+90^\circ$ , and  $+40^\circ$   $2\theta$  were used in subsequent data analysis. The space group  $Fd\bar{3}$  was employed for reason (a) given in section 3a.

## Structure Determination

(1) **Crystal 1, Na<sub>60</sub>(H<sub>3</sub>O)<sub>32</sub>(H<sub>2</sub>O)<sub>24</sub>Si<sub>100</sub>Al<sub>92</sub>O<sub>384</sub>.** Full-matrix least-squares refinement<sup>16</sup> was initiated using the framework coordinates of dehydrated Na-X.<sup>8</sup> These positions when refined isotropically yielded  $R_1 = 0.19$  and  $R_2 = 0.25$ , where  $R_1 = \sum |F_o - |F_c|| / \sum F_o$  and  $R_2 = (\sum w(F_o - |F_c|)^2 / \sum wF_o^2)^{1/2}$ .

A Fourier difference function yielded two strong peaks at (0.057, 0.057, 0.057) and (0.234, 0.234, 0.234), positions near framework oxygens normally occupied by cations. Anisotropic refinement of framework atoms and these two positions as Na<sup>+</sup> ions converged to  $R_1 = 0.058$  and  $R_2 = 0.097$ . The thermal parameter of Na at (0.060, 0.060, 0.060) was anomalously large ( $U_{iso} = 0.072$ ) and long. When it was split into two positions, it refined to Na(I') at (0.056, 0.056, 0.056) with an occupancy of 17.0(15) per unit cell and O(I') (representing hydronium ions) at (0.070, 0.070, 0.070) with an occupancy of 15.6(24). These occupancies were both fixed at 16 per unit cell. See Table 1a.

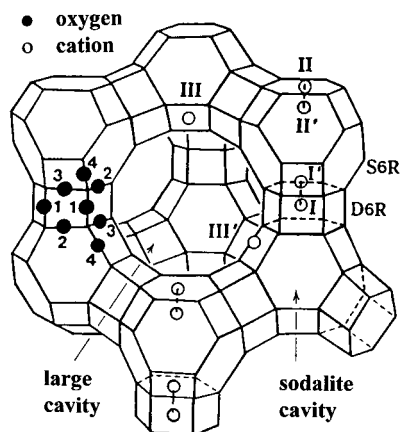
In the above, sodium and hydronium ions can be distinguished because 1) their approach distances to framework oxygens are different (Na, usually 2.2–2.4  $\text{\AA}$ ; H<sub>3</sub>O<sup>+</sup>, usually 2.6–2.8  $\text{\AA}$ ) and (2) the cation charges must sum to 92+ per unit cell; an alternative assignment of ionic identities usually does not allow the major positions to refine to acceptable occupancies.

An ensuing Fourier function revealed a strong peak on the 3-fold axis at (0.137, 0.137, 0.137) which refined as 9(2) O(5) atoms to  $R_1 = 0.057$  and  $R_2 = 0.095$ . Because O(5) is much too far from the framework (anionic) to be a cation, it should represent H<sub>2</sub>O molecules. However, O(5) should be on a 2-fold, not a 3-fold, axis because its environment has that symmetry: it can logically coordinate to two Na<sup>+</sup> ions at Na(I') and hydrogen bond to two hydronium ions at O(I'). The maximum occupancy at this position should be eight per unit cell (one per sodalite unit) to avoid the unacceptable maximum O(5)–O(5) distance of ca. 0.6  $\text{\AA}$ . Refinement of O(5) on the 2-fold axis with a fixed occupancy of eight converged to  $R_1 = 0.056$  and  $R_2 = 0.092$ .  $U_{11}$ ,  $U_{22}$ , and  $U_{12}$  of O(5) refined to large values with high esd's: 0.084(99), 0.215(215), and 0.107(47)  $\text{\AA}^2$ , respectively, indicating motion in the plane midway between the two ions at Na(I').  $U_{11}$  and  $U_{22}$  were constrained to be equal in subsequent refinements to reduce the number of O(5) parameters.

Two more peaks found at (0.190, 0.234, 0.419) and (0.178, 0.180, 0.419) refined as 16(2) O(III')s and 16(2) Na(III')s, respectively. See Table 1a. Refinement with both occupancies fixed at 16 converged to  $R_1 = 0.048$  and  $R_2 = 0.072$ .

Another peak found at (0.097, 0.142, 0.443) refined to 12.4(18) oxygens at O(6). O(6) is not close to any framework oxygen and is 2.29(13)  $\text{\AA}$  from Na(III'). It appears to be a water molecule bound to Na(III'), so its occupancy was constrained to be equal to that of Na(III'). The possibility that two water molecules coordinate to Na(III') was explored in refinement; it





**Figure 2.** Stylized drawing of the framework structure of zeolite X. Near the center of the each line segment is an oxygen atom. The nonequivalent oxygen atoms are indicated by the numbers 1–4. Silicon and aluminum atoms alternate at the tetrahedral intersections, except that Si substitutes for Al at about 4% of the Al positions in the crystal studied. Extraframework cation positions are labeled with Roman numerals. Site U (not shown) is at the center of the sodalite unit (0.125, 0.125, 0.125); site U' is anywhere near site U.

was dismissed because it led to an unreasonable O(6)–Na(III')–O(6) angle ( $46(4)^\circ$ ).

Finally, anisotropic least-squares refinement of all positional and thermal parameters, except those of Na(I'), O(I'), O(III'), Na(III'), and O(6) which were refined isotropically, converged to the error indexes  $R_1 = 0.043$  and  $R_2 = 0.059$ . The goodness-of-fit  $[\sum w(F_o - |F_c|)^2 / (m - s)]^{1/2}$  is 0.86, the number of observations  $m$  is 374, and the number of parameters  $s$  is 85. The largest maximum/minimum in the final difference function is  $0.4/-0.8 \text{ e}\text{\AA}^{-3}$ . Atomic scattering factors for Si, Al, O, and Na were used.<sup>17</sup> All scattering factors were modified to account for anomalous dispersion.<sup>18,19</sup>

The final refinement<sup>20</sup> was done using all 1180 reflections:  $R_1 = 0.056$  for the 497 reflections with  $F_o > 4\sigma(F_o)$ , corresponding to  $I > 2\sigma(I_o)$ , and  $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2\}^{1/2} = 0.160$  for 1180 reflections. This allowed the esd's to decrease to about 35% of their former values. The final structural parameters and selected interatomic distances and angles are presented in Tables 1a and 2.

**(2) Crystal 2,  $\text{Na}_{60}\text{H}_{32}\text{Si}_{100}\text{Al}_{92}\text{O}_{384}$ .** Full-matrix least-squares refinement was initiated with the atomic parameters of the framework atoms of dehydrated Na–X.<sup>8</sup> Anisotropic refinement converged to  $R_1 = 0.20$  and  $R_2 = 0.25$ . The initial difference Fourier function revealed three large peaks at (0, 0, 0), (0.051, 0.051, 0.051), and (0.231, 0.231, 0.231). These were stable in least-squares refinement as Na(I), Na(I'), and Na(II). Anisotropic refinement including these  $\text{Na}^+$  ions converged to  $R_1 = 0.111$  and  $R_2 = 0.129$ . Occupancy refinement converged at 5.2(6) Na(I), 21.7(11) Na(I'), and 34(3) Na(II). These values were reset and fixed at 5, 22, and 32  $\text{Na}^+$  ions at Na(I), Na(I'), and Na(II), respectively, because the adjacent site I and I' positions cannot be both occupied by  $\text{Na}^+$  ions (the distance between these two positions is  $2.05 \text{ \AA}$ , in accord with the established rule: (no. at I) + (no. at I')/2 = 16), and the maximum number of  $\text{Na}^+$  ions that can exist at Na(II) is 32.  $R_1$  and  $R_2$  converged to 0.111 and 0.128 at this point. A subsequent difference Fourier synthesis revealed a peak at (0.064, 0.061, 0.417) that was stable in refinement with a fixed thermal parameter. Its occupancy was fixed at two  $\text{Na}^+$  ions because the structure of crystal 1, consistent with the titration results (Figure 1), indicated that 60  $\text{Na}^+$  ions are present per unit cell. Refinement converged to  $R_1 = 0.110$  and  $R_2 = 0.124$ . No hydrogen ion positions were found

in the ensuing difference function, and refinements including hydrogen ions at calculated positions did not lead to lower error indexes. Refinements with partial occupancies at each of the four framework oxygens, exploring the proposition that the structure had lost many or all of its  $\text{H}^+$  ions with framework oxygens as water during dehydration, all yielded slightly higher error indexes.

In the penultimate cycles of least-squares refinement, all shifts in atomic parameters were less than 0.01% of their corresponding standard deviations. The final difference function was featureless. The goodness-of-fit is 1.25, the number of observations is 305, and the number of parameters is 66. The largest maximum/minimum in the final difference function is  $1.2/-1.8 \text{ e}\text{\AA}^{-3}$ .

The final refinement<sup>20</sup> was done using all 716 reflections:  $R_1 = 0.139$  for the 337 reflections with  $F_o > 4\sigma(F_o)$  and  $wR_2 = 0.324$ . The final structural parameters are presented in Table 1b and selected interatomic distances and angles are in Table 2.

These higher error indexes for crystal 2 are indicative of crystal damage. Two other crystals were prepared to see whether better diffraction data could be gathered. Unfortunately they were both less satisfactory than the first.

**(3) Powder Sample,  $\text{Na}_{54}(\text{D}_3\text{O})_{42}\text{Si}_{96}\text{Al}_{96}\text{O}_{384} \cdot \sim 80\text{D}_2\text{O}$ .** Refinement of the neutron data was performed with the program GSAS.<sup>21</sup> Positional parameters from a previous study were taken as the initial model for the framework Si, Al, and O atoms. Soft constraints of 1.61, 1.73, 2.63 and  $2.83 \text{ \AA}$  were applied to Si–O, Al–O, O–O(Si) and O–O(Al), respectively. The final average Si–O and Al–O distances were  $1.615(7)$  and  $1.731(6) \text{ \AA}$ , respectively. Early difference Fourier functions revealed scattering matter at site I', near site I', and at site II. These were assigned to oxygen, deuterium, and sodium on the basis of interatomic distances; the first two constitute the hydronium ions. After it was clear that these oxygen and deuterium positions had occupancy factors corresponding to a 1:3 atom ratio, further refinement was conducted with the ratio fixed at this value. Subsequent difference functions revealed scattering matter in the supercage near Na(II), at site II', near the center of the sodalite unit (site U') and at site I. The first three of these were assigned to oxygen (of water) and the latter to sodium. After refinement indicated near site-limit occupancies for Na(II), Ow1 (water oxygen bonded to Na(II)) and Ow(U'), their occupancy parameters were fixed at 1.0, 0.333, and 0.167 corresponding to 32, 32, and 8 per unit cell, respectively. Several positions at and near the site U position ( $x, x, x = 1/8$ ) were tried; the position found in the companion single-crystal study gave the best data fit.

The occupancy of site I by  $\text{Na}^+$  should be viewed with caution because of its low occupancy factor and the potential pitfalls of special-position refinement.

The refined parameters and selected geometry are presented in Tables 3 and 4, respectively. Additional details of the refinement, including plots of the observed and calculated diffraction profiles, are available as Supporting Information.

The final error indexes were  $wRp = 0.0316$  and  $\chi^2 = 9.93$ .

## Discussion

**(1) Description of Zeolite X.** Zeolite X is a synthetic counterpart of the naturally occurring mineral faujasite (see Figure 2). The 14-hedron with 24 vertexes known as the sodalite cavity or  $\beta$ -cage may be viewed as its principal building block. These  $\beta$ -cages are connected tetrahedrally at six-rings by bridging oxygens to give double six-rings (D6Rs, hexagonal

**TABLE 2: Selected Interatomic Distances and Angles**

	crystal 1	crystal 2 <sup>a</sup>
(a) Bond Distances (Å)		
Si—O(1)	1.634(5)	1.674(5)
Si—O(2)	1.644(6)	1.669(4)
Si—O(3)	1.658(5)	1.684(5)
Si—O(4)	1.640(5)	1.651(5)
mean	1.644	1.670
Al—O(1)	1.693(6)	
Al—O(2)	1.715(6)	
Al—O(3)	1.715(5)	
Al—O(4)	1.709(5)	
mean	1.708	
Na(I)—O(3)		2.675(14)
Na(I')—O(3)	2.342(6)	2.243(13)
Na(I')—O(2)	2.990(6)	2.973(11)
Na(I')—O(5)	2.722(22)	
O(I')—O(3)	2.50(3)	
O(I')—O(5)	2.94(4)	
Na(II)—O(2)	2.356(5)	2.362(12)
Na(II)—O(4)	2.917(5)	2.872(13)
O(III')—O(1)	2.65(3)	
O(III')—O(4)	2.79(3)	
O(III')—O(6)	2.93(6)	
Na(III')—O(4)	2.43(4)	2.52(6)
Na(III')—O(1)	2.84(5), 3.14(6)	2.92(3)
Na(III')—O(6)	2.49(9)	
O(5)—O(4)	2.78(5)	
O(6)—O(3)	2.967(12)	
(b) Bond Angles (deg)		
O(1)—Si—O(2)	113.1(3)	112.2(5)
O(1)—Si—O(3)	111.6(3)	108.7(6)
O(1)—Si—O(4)	107.1(3)	109.5(6)
O(2)—Si—O(3)	106.1(3)	107.1(6)
O(2)—Si—O(4)	106.7(3)	105.6(6)
O(3)—Si—O(4)	112.2(3)	113.9(6)
O(1)—Al—O(2)	112.9(3)	
O(1)—Al—O(3)	110.9(3)	
O(1)—Al—O(4)	108.8(3)	
O(2)—Al—O(3)	106.5(3)	
O(2)—Al—O(4)	105.6(3)	
O(3)—Al—O(4)	112.1(3)	
O(3)—Na(I)—O(3)		90.0(4)
O(3)—Na(I')—O(3)	112.6(6)	114.7(5)
O(3)—Na(I')—O(5)	105.2(10)	
O(3)—O(I')—O(3)	98.1(10)	
O(3)—O(I')—O(5)	110.4(12)	
Na(I')—O(5)—Na(I')	135.4(12)	
Na(I')—O(5)—O(I')	106.1(3)	
O(I')—O(5)—O(I')	86.1(8)	
O(2)—Na(II)—O(2)	110.0(2)	113.6(3)
O(1)—O(III')—O(4)	57.9(5)	
O(1)—O(III')—O(6)	69.2(18)	
O(4)—Na(III')—O(1)	59.4(9)	59.5(10)
O(4)—Na(III')—O(6)	108(2)	
O(III')—O(6)—Na(III')	159(3)	

<sup>a</sup> Only mean (Si,Al) positions were determined.

prisms) and, concomitantly, an interconnected set of even larger cavities (supercages) accessible in three dimensions through 12-ring (24-membered) windows. The Si and Al atoms occupy the vertexes of these polyhedra. The oxygen atoms lie approximately midway between each pair of Si and Al atoms but are displaced from those points to give near-tetrahedral angles about Si and Al. Single six-rings (S6Rs) are shared by sodalite and supercages, and may be viewed as the entrances to the sodalite units. Each unit cell has eight sodalite units, eight supercages, 16 D6Rs, 16 12-rings, and 32 S6Rs.

Exchangeable cations, which balance the negative charge of the aluminosilicate framework, are found within the zeolite's cavities. They are usually found at the following sites shown in Figure 2: site I at the center of the D6R, site I' in the sodalite

**TABLE 3: Positional, Thermal, and Occupancy Parameters for Na<sub>54</sub>(D<sub>3</sub>O)<sub>42</sub>Si<sub>96</sub>Al<sub>96</sub>O<sub>384</sub> · ~ 80D<sub>2</sub>O at 10 K<sup>a</sup>**

atom	Wyc. position	x	y	z	U <sub>iso</sub>	occupancy <sup>b</sup>
Si	96(g)	-526(1)	1248(2)	344(2)	29.3(10)	96
Al	96(g)	-547(1)	386(1)	1267(2)	29.3(10)	96
O(1)	96(g)	-1078(1)	-3(2)	1049(2)	33.0(4)	96
O(2)	96(g)	-20(1)	-27(2)	1435(1)	33.0(4)	96
O(3)	96(g)	-341(1)	783(1)	745(2)	33.0(4)	96
O(4)	96(g)	-749(2)	747(2)	1822(2)	33.0(4)	96
O(I')	32(e)	703(3)	703(3)	703(3)	40.0	17.8(2)
D	96(g)	260(3)	748(4)	636(4)	50.0	53.4(2)
Na(II)	32(e)	2374(2)	2374(2)	2374(2)	35.0	32
Ow(U')	48(f)	1250	1250	1520	35.0	8
Ow(II')	32(e)	1847(4)	1847(4)	1847(4)	35.0	11.3(7)
Ow1	96(g)	2895(9)	3027(5)	2769(5)	35.0	32
Na(I)	16(c)	0	0	0	35.0	4.7(5)

<sup>a</sup>  $a = 25.0523(5)$  Å. Positional and thermal parameters (Å<sup>2</sup>) are given  $\times 10^4$ . Values without esd's were not varied in least-squares refinement.

<sup>b</sup> The occupancy is given as the number of atoms or ions per unit cell. Values given as integers were not varied in least-squares refinement.

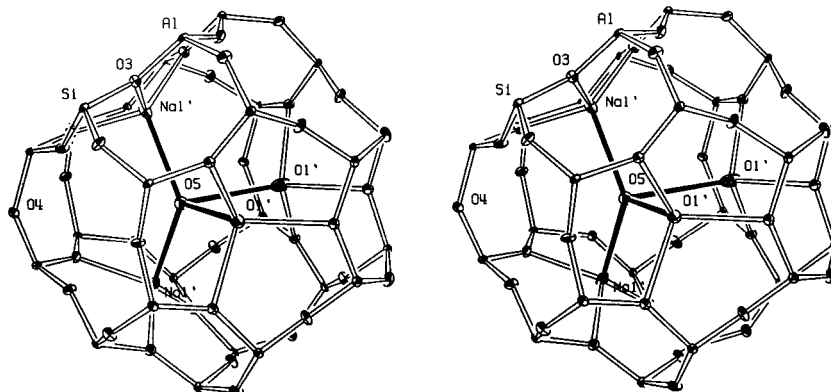
**TABLE 4: Selected Geometry for Na<sub>54</sub>(D<sub>3</sub>O)<sub>42</sub>Si<sub>96</sub>Al<sub>96</sub>O<sub>384</sub> · ~ 80D<sub>2</sub>O at 10 K**

mean Si—O	1.615(7)
mean Al—O	1.731(6)
mean O—O at Si	2.63(6)
mean O—O at Al	2.83(3)
O(I')—O(3)	2.625(8)
O(I')—D	1.128(11)
D—O(3)	1.532(8)
D—D	1.567(15)
O(I')—Ow(U')	2.818(15)
D—O(I')—D	88.1(6)
O(I')—D—O(3)	161.0(10)
Na(II)—O(2)	2.411(5)
Na(II)—Ow(II')	2.286(21)
Na(II)—Ow1	2.316(15)
Na(I)—O(3)	2.839(4)
Ow(II')—O(2)	2.609(10)
Ow(II')—O(I')	2.871(15)

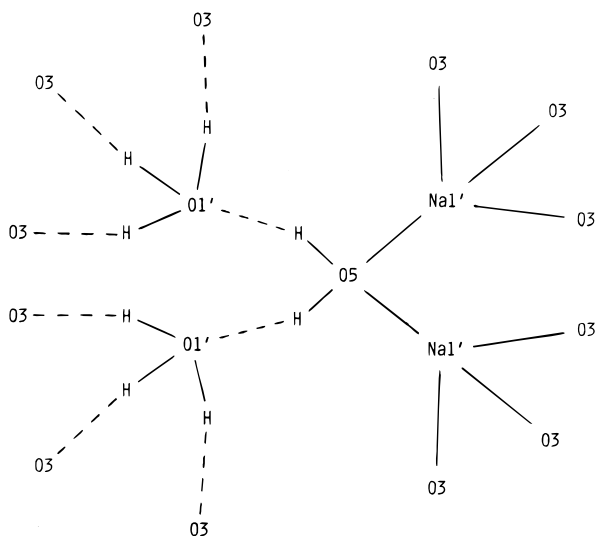
cavity on the opposite side of either of the D6R's six-rings from site I, site II' inside the sodalite cavity near a S6R, site II at the center of the S6R or displaced from this point into a supercage, III in the supercage on a 2-fold axis opposite a four-ring between two 12-rings, and III' somewhat off III (off the 2-fold axis). The position at the center of the sodalite unit, site U, is sometimes occupied by cations.

**(2) Crystal 1, Na<sub>60</sub>(H<sub>3</sub>O)<sub>32</sub>(H<sub>2</sub>O)<sub>24</sub>Si<sub>100</sub>Al<sub>92</sub>O<sub>384</sub>.** In this structure, sodium ions are found at three different crystallographic sites, hydronium ions at two, and water molecules at two. Two different I' positions are occupied by 16 Na<sup>+</sup> and 16 H<sub>3</sub>O<sup>+</sup> ions, respectively, per unit cell; a water molecule bridges between two of each in each sodalite unit. Two different III' sites are occupied by 16 Na<sup>+</sup> and 16 H<sub>3</sub>O<sup>+</sup> ions, respectively, per unit cell; 16 water molecules in the supercages each bridge between a Na<sup>+</sup> and an H<sub>3</sub>O<sup>+</sup> ion. The remaining 28 Na<sup>+</sup> ions are found at site II. It may be expected that site II would be fully occupied in LSX.

The Na(I') and O(I') cations occupy two sites I'. Two Na<sup>+</sup> ions at Na(I') and two H<sub>3</sub>O<sup>+</sup> ions at O(I') are arranged nearly tetrahedrally within each sodalite cavity. One water at O(5) near the sodalite center coordinates to both Na<sup>+</sup> ions at 2.72(2) Å and hydrogen bonds to both hydronium ions at 2.94(4) Å to give a grouping that may be viewed as a (H<sub>3</sub>O<sup>+</sup>)<sub>2</sub>H<sub>2</sub>O(Na<sup>+</sup>)<sub>2</sub> cluster filling each sodalite cavity (see Figures 3 and 4). The Na(I')—O(3) distances are 2.329(15) Å, somewhat longer than the corresponding distances in the crystal structures of dehy-



**Figure 3.** Stereoview of a sodalite cavity. Two  $\text{Na}^+$  ions at  $\text{Na(I')}$  lie at site I' and two  $\text{H}_3\text{O}^+$  ions at  $\text{O(I')}$  lie at another site I'. They are arranged tetrahedrally and are bound to a water molecule at  $\text{O(5)}$  near the center of the sodalite cavity. The contents of the sodalite unit may be viewed as a  $(\text{H}_3\text{O}^+)_2\text{H}_2\text{O}(\text{Na}^+)_2$  cluster. Ellipsoids of 20% probability are shown.



**Figure 4.** Schematic view of the  $(\text{H}_3\text{O}^+)_2\text{H}_2\text{O}(\text{Na}^+)_2$  cluster. Each  $\text{Na}^+$  ion at  $\text{Na(I')}$  binds to three framework oxygens at  $\text{O(3)}$  and coordinates to a water molecule at  $\text{O(5)}$ . Each  $\text{H}_3\text{O}^+$  ion at  $\text{O(I')}$  hydrogen bonds to three framework oxygens at  $\text{O(3)}$  and hydrogen bonds further via its lone pair to a hydrogen atom of the same  $\text{O(5)}$  water molecule.

hydrated  $\text{Na-X}$  ( $2.276(9)$  Å)<sup>8,9</sup> and those of  $\text{Na-X}$  containing linear  $\text{Na}_3^{2+}$  clusters ( $2.242(7)$  Å),<sup>22</sup> probably because of the higher coordination number (four) of  $\text{Na}^+$  ions at site I' in this structure.  $\text{O(I')}$  lies relatively farther inside the sodalite cavity than  $\text{Na(I')}$  because  $\text{H}_3\text{O}^+$  is larger than  $\text{Na}^+$ .

Sixteen  $\text{Na}^+$  and 16  $\text{H}_3\text{O}^+$  are found at two different III' sites (see Figure 5). Each of the 16  $\text{Na}^+$  ions at  $\text{Na(III')}$  binds to two framework oxygens (to  $\text{O(4)}$  at  $2.42(9)$  Å and to  $\text{O(1)}$  at  $2.91(9)$  Å) and is coordinated at  $2.49(9)$  Å by one water molecule at  $\text{O(6)}$ . Each of the 16  $\text{H}_3\text{O}^+$  ions at  $\text{O(III')}$  also binds to two framework oxygens (to  $\text{O(1)}$  at  $2.62(8)$  Å and to  $\text{O(4)}$  at  $2.80(8)$  Å), and hydrogen bonds at  $2.93(6)$  Å to the same  $\text{O(6)}$  molecule.  $\text{O(6)}$  can hydrogen bond at  $2.97(1)$  Å to a framework oxygen,  $\text{O(3)}$ . This or similar bridging in the fully hydrated structure may be responsible for the equal and stoichiometric occupancies at  $\text{O(III')}$  and  $\text{Na(III')}$ .

Site II, a 32-fold position, is occupied by the remaining 28.4(10) cations per unit cell, all  $\text{Na}^+$  ions (see Figure 5). The  $\text{Na(II)-O(2)}$  distances are  $2.367(9)$  Å, very similar to those found in the structures of dehydrated  $\text{Na-X}$  ( $2.343(5)$  Å)<sup>8,9</sup> and  $\text{Na-X}$  containing linear  $\text{Na}_3^{2+}$  clusters ( $2.363(8)$  Å).<sup>21</sup>

**(3) Crystal 2,  $\text{Na}_{60}\text{H}_{32}\text{Si}_{100}\text{Al}_{92}\text{O}_{384}$ .** Sixty  $\text{Na}^+$  ions are found at three different crystallographic sites. Neither  $\text{H}_3\text{O}^+$  ions nor

$\text{H}_2\text{O}$  molecules are found. Vacuum dehydration at  $150$  °C had sufficed to remove all  $\text{H}_2\text{O}$  molecules from the hydrated crystal and to decompose all  $\text{H}_3\text{O}^+$  ions.

Five  $\text{Na}^+$  ions are found at site I at the centers of the D6R's. The octahedral distance,  $2.675(14)$  Å, is a little shorter than the corresponding bond distance in the previously determined single-crystal structure of dehydrated  $\text{Na-X}$ ,  $2.748(5)$  Å.<sup>8</sup> About 22  $\text{Na}^+$  ions ( $\text{Na(I')}$ ) are found at site I'. The  $\text{Na(I')-O(3)}$  distance,  $2.243(13)$  Å, is shorter than that in crystal 1,  $2.328(15)$  Å, due to the removal of the water molecule near the center of the sodalite cage. Thirty-two  $\text{Na}^+$  ions at  $\text{Na(II)}$  fill site II in the supercage adjacent to S6Rs. The  $\text{Na(II)-O(2)}$  distance,  $2.362(12)$  Å, is the same as in crystal 1,  $2.367(9)$  Å. The remaining two  $\text{Na}^+$  ions are at a III' site.

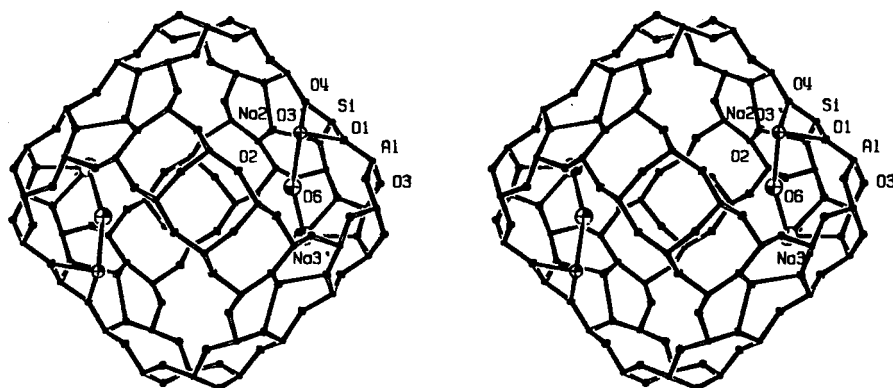
The 32  $\text{H}^+$  ions necessary to balance the negative charges of the zeolite framework could not be located. However, their positions are well-established crystallographically.<sup>23-30</sup> They are generally distributed among two positions, bound to  $\text{O(3)}$  in the sodalite cavity and to  $\text{O(1)}$  in the supercage. To avoid impossibly short  $\text{H}^+-\text{Na(I')}$  distances, no more than 10 can be in the sodalite cavities; each  $\text{H}^+$  could coordinate to an  $\text{O(3)}$  that does not coordinate to an ion at  $\text{Na(I')}$ . The remaining 22 or more  $\text{H}^+$  ions should be in the supercages, each of them coordinating to an  $\text{O(1)}$  oxygen.

**(4) Powder,  $\text{Na}_{54}(\text{D}_3\text{O})_{42}\text{Si}_{96}\text{Al}_{96}\text{O}_{384} \sim 80\text{D}_2\text{O}$ .** The neutron-diffraction study was done primarily to determine the geometry of the hydronium ions and their siting in the zeolite (Tables 3 and 4). Each sodalite cage contains two hydronium ions at site I', as in crystal 1. The oxygen of each deuterated hydronium ion bonds to its three deuterons at a distance of  $1.13(1)$  Å. Each deuteron also hydrogen bonds to an  $\text{O(3)}$  framework oxygen at  $1.53(1)$  Å (see Figure 6). These values may be compared with the values  $1.13$  and  $1.50$  Å found by Smith et al. for the corresponding distances in a deuterated hydronium ion interacting similarly with partially hydrated HSAPO-34.<sup>31</sup> Each hydronium ion also hydrogen bonds to a water molecule at the U' site, near the center of the sodalite unit, at a distance of  $2.82(2)$  Å. The oxygen positions are qualitatively the same as those found in crystal 1.

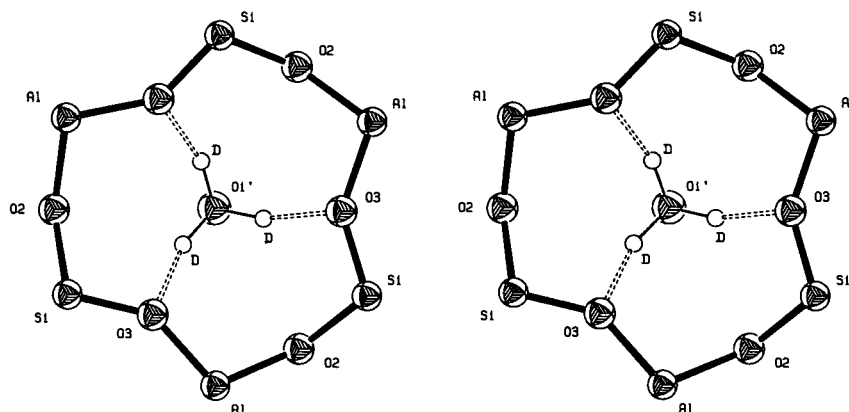
Sodium ions completely fill site II. Each  $\text{Na}^+$  bonds to three  $\text{O(2)}$  framework oxygens at  $2.41(1)$  Å and to a water oxygen,  $\text{Ow1}$ , at  $2.32(2)$  Å.  $\text{Ow1}$  lies off the 3-fold axis suggesting further bonding to  $\text{Na}^+$  and/or to water; these latter species were not detected suggesting that there may be more than one arrangement.

Scattering matter corresponding to 1.4 oxygen atoms per sodalite unit, 11 per unit cell, was observed in site II',  $2.29(2)$





**Figure 5.** Stereoview of the supercage. Four  $\text{Na}^+$  ions at Na(II) lie at site II and are arranged tetrahedrally. Two  $\text{H}_3\text{O}^+$  ions at O(III') lie at site III' and two  $\text{Na}^+$  ions at Na(III') lie at another site III'. Two times per supercage, a water molecule at O(6) bridges between O(III') and Na(III') to give a  $(\text{H}_3\text{O}^+(\text{H}_2\text{O})(\text{Na}^+))$  cluster. Ellipsoids of 20% probability are shown.



**Figure 6.** Stereoview of a  $\text{D}_3\text{O}^+$  ion at site I'. The D—O distance is 1.128(11) Å. Each deuteron hydrogen bonds to an O(3) framework oxygen at 1.532(8) Å. Ellipsoids of 20% probability are shown.

Å from Na(II) and 2.61(1) Å from the site II O(2) oxygen atom. The former is close to the sum of the ionic radii, e.g. 2.35 Å. While this species could hydrogen bond to a hydronium ion oxygen at a distance of 2.87(2) Å, the latter already has four hydrogen bonding interactions. In view of this and the short O—O distance of 2.61(1) Å to O(2), this species should be regarded as provisional requiring further verification.

The O(III'), Na(III'), and O(6) positions in single crystal 1 were not observed in this structure. One or more of the following factors may contribute to these differences: (a) small but definite differences in composition, e.g., (Si/Al = 96/96 versus 100/92, 52 versus 60  $\text{Na}^+$  ions per unit cell, and 80 versus 24  $\text{H}_2\text{O}$  molecules per unit cell, respectively, for powder X and crystal 1, respectively, and (b) data at 10 K versus 293 K, respectively.

Another difference between these results and those of crystal 1 is the finding of 16  $\text{Na}^+$  per unit cell at site I' in crystal 1. The high precision of the latter makes this a high probability finding. Placing this species in the powder model resulted in a negative peak at this position in the difference function, suggesting that this is a real difference in the nonframework atom siting of these two materials; possible reasons for this difference were enumerated above.

**(5) General Discussion.** The numbers of  $\text{H}_3\text{O}^+$  and  $\text{Na}^+$  ions found in the two single-crystal structures agree nicely with the results of the titration experiment. Apparently the difference in  $\text{Na}^+$  concentration has had little effect: it was 0.10 M for the single crystals and 0.011 M at pH = 6.35 in the titration. Of the 32  $\text{H}_3\text{O}^+$  ions found per unit cell in crystal 1, 16 occupy site I' and the other 16 are at III' positions.

The high selectivity of aluminosilicate zeolites for hydronium ions must involve the three strong hydrogen bonds that each  $\text{H}_3\text{O}^+$  ion can form with framework oxygen atoms. The similar excess charge magnitudes of the hydronium hydrogens (each formally 1/3+) and the framework oxygens (each formally about  $-96/384 = -0.25$ ) nearly allow local charge balance. (The excess charge has been distributed among the hydronium hydrogens and the framework oxygens in this simple calculation. A theoretical basis for this assignment of charges exists.<sup>32</sup>)

An additional structural basis for the high selectivity of zeolite X for  $\text{H}_3\text{O}^+$  may be seen in these results: water molecules, made more acidic by coordination to  $\text{Na}^+$ , can hydrogen bond to  $\text{H}_3\text{O}^+$  lone pairs of electrons. This is seen in the sodalite unit  $(\text{H}_3\text{O}^+)_2\text{H}_2\text{O}(\text{Na}^+)_2$  and in the supercage  $(\text{H}_3\text{O}^+)\text{H}_2\text{O}(\text{Na}^+)$ . The strengths of these interactions are indicated by the retention of these water molecules at 20 °C and  $1 \times 10^{-5}$  Torr. Other arrangements involving more water molecules may exist in fully hydrated  $\text{Na}_{60}(\text{H}_3\text{O})_{32}\text{Si}_{100}\text{Al}_{92}\text{O}_{384}$ .

## Summary

Na—X in equilibrium with 0.1 M  $\text{Na}^+$  solution at pH 6.35, evacuated at room temperature, contains 32 hydronium ions per unit cell at sites I' and III' and 24 water molecules. Sixty  $\text{Na}^+$  ions per unit cell are found at sites I', II, and III'. Zeolite Na—X has a high selectivity for  $\text{H}_3\text{O}^+$  at near neutral pHs because each  $\text{H}_3\text{O}^+$  hydrogen bonds to three framework oxygens and because water-bridged clusters of  $\text{Na}^+$  and  $\text{H}_3\text{O}^+$  can form. Upon evacuation at 150 °C, all water molecules are lost and all  $\text{H}_3\text{O}^+$  ions are decomposed. The 60  $\text{Na}^+$  ions are now found at

sites I, I', II, and III'. At least 20 of the 32 H<sup>+</sup> ions per unit cell should be in the supercage. By neutron diffraction, the positions of the deuterium atoms of the D<sub>3</sub>O<sup>+</sup> ions in the sodalite unit have been determined: D–O = 1.13(1) Å and D···O(framework) = 1.53(1) Å.

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**Supporting Information Available:** Observed and calculated structure factors squared with esd's for Na<sub>60</sub>(H<sub>3</sub>O)<sub>32</sub>·(H<sub>2</sub>O)<sub>24</sub>Si<sub>100</sub>Al<sub>92</sub>O<sub>384</sub> and Na<sub>60</sub>H<sub>32</sub>Si<sub>100</sub>Al<sub>92</sub>O<sub>384</sub>. Diffraction and refinement data; positional and occupancy parameters; selected interatomic distances; and observed, calculated, and difference pulsed-neutron powder-diffraction profiles for Na<sub>54</sub>(D<sub>3</sub>O)<sub>42</sub>Si<sub>96</sub>Al<sub>96</sub>O<sub>384</sub> · ~ 80D<sub>2</sub>O. This information is available free of charge via the Internet at <http://pubs.acs.org>.

## References and Notes

- (1) Breck, D. W.; Eversole, W. G.; Milton, R. M.; Reed, T. B.; Thomas, T. L. *J. Am. Chem. Soc.* **1956**, *78*, 5963.
- (2) Baes, Jr., C. F.; Mesmer, R. E. *The Hydrolysis of Cations*; Wiley: New York, 1976.
- (3) Cook, T. E.; Cilley, W. A.; Savitsky, A. C.; Wiers, B. H. *Environ. Sci. Technol.* **1982**, *16*, 344.
- (4) O'Connor, J. F.; Townsend, R. P. *Zeolites* **1985**, *5*, 158.
- (5) Drummond, D.; De Jonge, A.; Rees, L. V. C. *J. Phys. Chem.* **1983**, *87*, 7, 1967.
- (6) Franklin, K. R.; Townsend, R. P.; Whelan, S. J.; Adams, C. J. *Proceedings of the 7th International Zeolite Conference*; Elsevier: Amsterdam, 1986; p 289.
- (7) Harjula, R.; Lehto, J.; Pothuis, J. H.; Dyer, A.; Townsend, R. P. *Proceedings of the 11th International Conference on Ion Exchange*, Elsevier: Amsterdam, 1991; p 157.
- (8) Olson, D. H. *Zeolites* **1995**, *15*, 439.
- (9) Vitale, G.; Mellot, C. F.; Bull, L. M.; Cheetham, A. K. *J. Phys. Chem.* **1997**, *101*, 4559.
- (10) Zhu, L.; Seff, K. *J. Phys. Chem. B* **1999**, *103*, In press.
- (11) Kühl, G. H.; Schweizer, A. E. *J. Catal.* **1975**, *38*, 469.
- (12) Bogomolov, V. N.; Petranovskii, V. P. *Zeolites* **1986**, *6*, 418.
- (13) Loewenstein, W. *Am. Mineral.* **1954**, *39*, 92.
- (14) Bae, D.; Seff, K. *Micro. Meso. Mater.* Submitted for publication.
- (15) Peterson, B. K. *J. Phys. Chem. B* **1999**, *103*, 3145.
- (16) *SHELXTL-PC*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1990.
- (17) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 73.
- (18) Reference 17, p 149.
- (19) Cromer, D. T. *Acta Crystallogr.* **1965**, *18*, 17.
- (20) Sheldrick, G. M. *SHELXL93, Program for the Refinement of Crystal Structures*; University of Göttingen: Germany, 1993.
- (21) Larson, A. C.; Von Dreele, R. B. General structure analysis system-GSAS. Report No. LA-UR 86-748; Los Alamos National Laboratory: Los Alamos, 1994.
- (22) Shibata, W.; Seff, K. *J. Phys. Chem. B* **1997**, *101*, 9022.
- (23) Mortier, W. J. *Compilation of Extraframework Sites in Zeolites*, Butterworth: Guildford, U.K., 1982.
- (24) Olson, D. H.; Dempsey, E. J. *J. Catal.* **1969**, *13*, 22.
- (25) Mortier, W. J.; Pluth, J. J.; Smith, J. V. *J. Catal.* **1976**, *45*, 367.
- (26) Jirak, Z.; Vratislav, S.; Bosadek, V. *J. Phys. Chem.* **1980**, *41*, 1089.
- (27) Cheetham, A. K.; Eddy, M. M.; Thomas, J. M. *J. Chem. Soc., Chem. Commun.* **1984**, 1337.
- (28) Czjzek, M.; Jobic, H.; Fitch, A. N.; Vogt, T. *J. Phys. Chem.* **1992**, *96*, 1535.
- (29) Sun, T.; Seff, K. *J. Catal.* **1992**, *138*, 405.
- (30) Sun, T.; Seff, K. *J. Phys. Chem.* **1993**, *97*, 7719.
- (31) Smith, L.; Cheetham, A. K.; Morris, R. E.; Marchese, L.; Thomas, J. M.; Chen, J. *Science* **1996**, *271*, 799.
- (32) Fiedler, K.; Lohse, U.; Sauer, J.; Stach, H.; Schirmer, W. *Proceedings of the 5th International Zeolite Conference*, Heyden: London, 1980; p 494.