Structure of Dehydrated Zn²⁺-Exchanged Zeolite X. Overexchange, Framework Dealumination and Reorganization, Stoichiometric Retention of Monomeric Tetrahedral Aluminate

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Complete Zn^{2+}-exchange of a single crystal of zeolite X ($Na_{92}Si_{100}Al_{92}O_{384}$, space group $Fd\bar{3}$) was attempted at 80 °C from aqueous solution (pH = 5.2 at 23 °C). After dehydration at 400 °C and ca. 1×10^{-5} Torr for 2 days, its structure was determined by X-ray diffraction techniques in its new cubic space group $Fd\bar{3}m$ at 23 °C ($a = 24.718(6)$ Å). It was refined to the final error index $R_1 = 0.119$ with 183 reflections for which $F_o > 4\sigma(F_o)$. About 56 Zn^{2+} ions occupy three crystallographic sites: 30 almost fill site I′, 23 nearly three-quarters fill site II′, and the remaining three occupy site II. Each sodalite unit contains a monomeric tetrahedral aluminate anion (Al–O = 1.79(6) Å) at its center; this appears to be the first accurate crystallographic observation of the monomeric tetrahedral aluminate ion. Many are $HAlO_4^{4-}$ anions each coordinated by seven Zn^{2+} ions: three of the four aluminate oxygens each bridge between a site-I′ Zn^{2+} and a site-II′ Zn^{2+} ion; the aluminate OH group coordinates only to a site-I′ Zn^{2+} cation. Other AlO_4^{5-} ions may have fewer Zn^{2+} and more H^+ ions. Dealumination of the zeolite framework and its subsequent reorganization to remove the resulting vacancies occurred during the dehydration step, not during ion exchange. The number of unit cells in the crystal decreases in this process and long-range Si/Al ordering is lost, resulting in a change of space group.

Introduction

Anhydrous aluminosilicate zeolites contain coordinatively unsaturated cations. This unsaturation can be satisfied by sorption: sorbed species usually prefer to coordinate to these cations. When the sorbed species are atoms of the same element as the cations, their electrons may be redistributed to form cationic clusters (such as Cd_2^{2+}, K_4^{3+}, and Na_3^{2+})[1] and cationic continua (such as Cs_{122}^{86+} per unit cell).[1] Atoms (such as In or Na), atomic clusters (such as Cd_2), and partially reduced monatomic cations (such as Cd^+) have also been found crystallographically in the zeolite.[1]

Not many metals have enough vapor pressure for gas-phase sorption into zeolites at temperatures at which the zeolite is stable (below 700 to ca. 1000 °C, depending upon the zeolite type and its state of ion exchange). One sufficiently volatile metal whose sorption chemistry into zeolites remains relatively unexplored is Zn.

Applications of Zn-containing zeolites can be environmentally safe because Zn is a nontoxic element. In fact, Zn is an essential nutrient for all plants and animals, especially during gestation. Zinc already plays a role in industrial hydrocarbon catalysis,[2-7] e.g., the conversion of butane into aromatics,[8] basic alkene isomerization,[9,10] hydrosulfurization of alcohols,[11] decomposition of nitromethane,[12] and the separation of hydrogen sulfide from fossil fuels.[13]

Complete ion exchange and full dehydration are desirable for crystallographic analysis. The product zeolite can then have relatively high, possibly stoichiometric, occupancies at its nonframework positions. With fewer atomic positions and all atoms firmly held, such structures are relatively simple to solve and to describe.

Zn^{2+} was fully exchanged into zeolite A from aqueous solution, and the structures of hydrated and largely dehydrated single crystals were determined crystallographically.[14] Although hexaaquo–Zn^{2+} ions were reported at sodalite-unit centers in the hydrated zeolite, they are likely to be hydrolyzed, perhaps to $Zn(OH)_2(H_2O)_4$; otherwise Zn^{2+} cations should coordinate directly to framework oxygens for electrostatic reasons. This would explain why residual oxygens coordinated to Zn^{2+} were always found in the zeolite upon attempted dehydration.[14] This zeolite may contain ZnO clusters such as those currently thought to be important for the catalytic conversion of light hydrocarbons to aromatics in HZSM zeolites.[15]

Recently, fully dehydrated single crystals of Zn^{2+}-exchanged zeolite X were prepared by ion exchange using an aqueous solution at 23 °C. After vacuum dehydration at 400 °C, their structures were determined by X-ray diffraction methods.[16] In all cases over-exchange of $Zn(OH)_2$ appears to have occurred; 54 Zn^{2+} ions were found per unit cell, eight more than required to balance the anionic charge of the zeolite framework. After dehydration, one nonframework oxide ion coordinating to an otherwise three-coordinate six-ring Zn^{2+} ion was found deep within each sodalite unit.

It was with the hope of avoiding this over-exchange, to prepare stoichiometrically exchanged Zn_{46}-X, that exchange at a higher temperature, 80 °C, was attempted.

Crystal Preparation

Large single crystals of sodium zeolite X, stoichiometry $Na_{92}Si_{100}Al_{92}O_{384}$ per unit cell, were prepared in Leningrad, now St. Petersburg, Russia.[17] One of these, a colorless octahedron about 0.14 mm cross-section, was lodged in a fine Pyrex capillary. Ion exchange was accomplished at 80 °C by allowing an aqueous solution of 0.05 M $Zn(NO_3)_2 \cdot 6H_2O$ (Fisher Chemical, ACS grade, pH = 5.2 at 23 °C) to flow past the crystal as described in Table 1. After the ion-exchange process was

TABLE 1: Summary of Experimental Data

crystal cross-section (mm)	0.14	2θ range in data collcn (deg)	3−45
ion exchange T (°C)	80	no. of reflns gathered	3519
ion exchange t (days)	2	no. of unique reflns (m)	517
flow rate (mm/s)	4	no. of reflns with $F_o > 4\sigma(F_o)$	183
desolvation T (°C)	400	no. of params (s)	50
data collection T (°C)	23	data/param ratio (m/s)	10.3
scan technique	$\theta-2\theta$	merging R (all intensities)	0.54
radiation (Mo Kα)			
λ_1 (Å)	0.70930	weighting param: a/b	0.0/950.3
λ_2 (Å)	0.71359		
unit-cell constant, a_o (Å)	24.718(6)	$R_1{}^a$	0.119
2θ range for a_o (deg)	14−16	$wR_2{}^b$	0.213
no. of reflns for a_o	16	goodness of fit^c	1.30

^{a} $R_1 = \sum(|F_o - |F_c||)/\sum F_o$ is calculated using $F_o > 4\sigma(F_o)$. ^{b} $wR_2 = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum w(F_o{}^2)^2\}^{1/2}$ is calculated using all intensities. ^{c} GOOF $= \{\sum[w(F_o{}^2 - F_c{}^2)^2]/(m - s)\}^{1/2}$.

finished, the crystal appeared dry and was not washed further. The tip of the capillary was then sealed by torch to allow the crystal to be vacuum dehydrated.

A buffer of zeolite 5A pellets was placed in series between the capillary containing the crystal and the vacuum system. Two horizontal, end-to-end cylindrical ovens were placed about the buffer and the crystal, respectively, so that the temperature of the crystal and the buffer could be controlled independently. The system was allowed to dehydrate under a dynamic vacuum of ca. 1×10^{-5} Torr for 24 h. The temperature of the zeolite buffer was then increased to 350 °C, while the crystal temperature was slowly raised in increments of ca. 5 °C/h to 150 °C, and then in increments of ca. 10 °C/h to 400 °C. After 48 h, the buffer oven was allowed to cool first so it could act as a sorbant, protecting the crystal from small molecules, in particular water, that might otherwise migrate to the crystal from more distant, not baked out, regions of the vacuum system. After cooling, the crystal, still under vacuum, was sealed off in its capillary by torch. The crystal had changed its appearance from colorless to bright white.

X-ray Diffraction

The cubic space group $Fd\bar{3}m$ was used throughout this work. It was justified (a) by its reflection conditions (*hkl*: $h + k, k + l, l + h = 2n$; *0kl*: $k + l = 4n$) and (b) by the intensity equality observed for *hkl* and *khl* reflections. This indicates that the space group $Fd\bar{3}$ (typical of the crystals in this batch[17]) is no longer appropriate after the treatment given to this crystal and that the long-range Si/Al ordering presumed present initially has been lost.

The unit cell constant at 23 °C, determined by least-squares refinement of selected intense reflections, is given in Table 1 together with other data describing the diffraction work.

Structure Determination

Full-matrix least-squares refinement[18] was initiated with the atomic positions of the framework atoms [(Si,Al), O(1), O(2), O(3), and O(4)] in the structure of fully dehydrated, fully Zn^{2+}-exchanged zeolite Y.[19] Since the SiO$_4$ and AlO$_4$ tetrahedra are indistinguishable in the space group $Fd\bar{3}m$, only the average species, (Si,Al), is considered in this work.

Isotropic refinement of the zeolite framework with fixed weighting scheme parameters converged to $R_1/wR_2 = 0.47/0.85$. (These error indices are defined in footnotes to Table 1.) A difference Fourier function revealed a large peak at (0.20, 0.20, 0.20). Isotropic refinement of framework atoms including this as Zn^{2+} ions at Zn(II′) converged to $R_1/wR_2 = 0.33/0.73$. An

ensuing Fourier function revealed a strong peak at (0.06, 0.06, 0.06); it refined quickly as Zn^{2+} ions at Zn(I′) to $R_1/wR_2 = 0.171/0.440$.

From a subsequent difference Fourier function, a peak of height 5.9 e Å^{-3} was found at (0.125, 0.125, 0.124). As oxide, this peak was too far from Zn^{2+} ions; as Zn^{2+} ions, its occupancy was less than 3. At this point we learned from Grey and Ciraolo that their solid-state NMR work on dehydrated Zn^{2+}-exchanged zeolite LSX had shown that aluminate ions, essentially unperturbed from tetrahedral, had been found in the sodalite units and that structure determination by powder crystallography had supported this result.[20] Isotropic refinement including this peak as Al^{3+} ions at Al(U) converged to $R_1/wR_2 = 0.157/0.403$ with 5.8(8) Al^{3+} ions per unit cell at the centers of the sodalite units. (Zeolites LSX, X, and Y all have the same framework structure, that of faujasite. They differ only in Si/Al ratio.)

Two more peaks found at (0.229, 0.229, 0.229) and (0.0815, 0.0815, 0.1521) were refined isotropically as Zn(II) and O(5), respectively, to $R_1/wR_2 = 0.129/0.391$. The occupancy at O(5) was constrained to 4 times that at Al(U) (see Table 2) to which it is bound tetrahedrally (Table 3). However, the geometry about Al(U) remained severely and unrealistically distorted. In an attempt to improve this geometry and to obtain the undistorted (according to NMR) aluminate ions found by Grey et al.,[20] the positional parameters at O(5) were allowed to refine off their mirror plane. O(5) converged nicely to (0.0673, 0.0832, 0.1342), and oxygens could be placed at low occupancy in this equipoint to give undistorted tetrahedral AlO$_4$ groups (see Tables 2 and 3). Refinement converged to $R_1/wR_2 = 0.129/0.311$.

Finally, anisotropic refinement of the framework atoms, Zn(I′) and Zn(II′), with isotropic refinement at the remaining positions, converged to $R_1/wR_2 = 0.119/0.213$ with improved weighting-scheme parameters. The possibility that Al(U) is octahedral was dismissed because R_1/wR_2 became 0.117/0.286 when a 6:1 O:Al constraint was used. Also, the best possible octahedron was severely irregular.

All shifts in the final cycles of refinement were less than 0.01% of their corresponding standard deviations. The largest peak (0.70 e Å^{-3}) on the final difference Fourier function was not stable in least squares. The second largest peak (0.65 e Å^{-3}) was not within bonding distance of any other atom and was not considered further. The third largest peak (0.52 e Å^{-3}) was too close to O(2) (0.93 Å).

Refinement with the occupancies of the nonframework ions in the sodalite unit (Zn(I′), Zn(II′), Al(U), and O(5)) constrained to a 4:3:1:4 stoichiometry converged with no change in error indices. Refinement with these occupancies fixed at 32, 24, 8, and 32, corresponding to an ideal full stoichiometry, caused the error indices to increase sharply to $R_1/wR_2 = 0.123/0.220$,

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TABLE 2: Positional,^{a} Thermal,^{a} and Occupancy Parameters

atom	Wyc pos	site	x	y	z	U_{11} or U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	occupancy^b
Si,Al	192(i)		−507(2)	371(3)	1238(3)	393(44)	311(39)	295(39)	21(34)	−150(51)	−100(35)	192
O(1)	96(h)		−1010(7)	1010(7)	0^c	546(104)	546(104)	323(142)	−346(127)	−92(77)	−92(77)	96
O(2)	96(g)		22(6)	22(6)	1517(7)	420(81)	420(81)	86(115)	99(122)	−43(68)	−43(68)	96
O(3)	96(g)		1782(6)	1782(6)	−184(9)	278(96)	278(96)	761(205)	78(132)	−25(93)	−25(93)	96
O(4)	96(g)		1699(6)	1699(6)	3227(9)	285(82)	285(82)	582(116)	58(107)	−111(88)	−111(88)	96
Zn(I′)	32(e)	I′	575(3)	575(3)	575(3)	778(53)	778(53)	778(53)	113(39)	113(39)	113(39)	29.1(9)
Zn(II′)	32(e)	II′	2024(3)	2024(3)	2024(3)	237(43)	237(43)	237(43)	73(38)	73(38)	73(38)	22.7(8)
Zn(II)	32(e)	II	2277(23)	2277(23)	2277(23)	323(332)						3.2(9)
Al(U)	8(a)	U	1250^c	1250^c	1250^c	551(169)						7.9(7)
O(5)	192(i)		673(27)	832(27)	1342(21)	164(248)						32(3)

^{a} Positional and thermal parameters are given × 10^4. Numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding parameter. 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})]. ^{b} Occupancy factors are given as the number of atoms or ions per unit cell. The occupancies for the first five positions (the zeolite framework) were held fixed in least-squares refinement. The occupancies of the last five positions refined freely in least squares with the exception of the constraint that Al:O(5) = 1:4. ^{c} Fixed by symmetry.

TABLE 3: Selected Interatomic Distances (Å) and Angles (deg)^a

framework		framework and nonframework	
(Si,Al)−O(1)	1.646(10)	Zn(I′)−O(3)	1.949(25)
(Si,Al)−O(2)	1.712(11)^b	Zn(II′)−O(2)	2.019(22)
(Si,Al)−O(3)	1.733(14)^b	Zn(II)−O(2)	2.00(3)
(Si,Al)−O(4)	1.642(10)	Al(U)−O(5)	1.79(6)
		Zn(I′)−O(5)	2.00(6)
O(1)−(Si,Al)−O(2)	115.9(8)	Zn(II′)−O(5)	1.97(6)
O(1)−(Si,Al)−O(3)	111.6(12)		
O(1)−(Si,Al)−O(4)	111.1(12)	O(3)−Zn(I′)−O(3)	108.4(7)
O(2)−(Si,Al)−O(3)	101.1(11)	O(2)−Zn(II′)−O(2)	112.5(7)
O(2)−(Si,Al)−O(4)	106.8(12)	O(2)−Zn(II)−O(2)	113.9(20)
O(3)−(Si,Al)−O(4)	109.8(11)	O(3)−Zn(I′)−O(5)	83.2(23), 96.6(23), 146.5(19)
		O(2)−Zn(II′)−O(5)	80.8(19), 109.5(25), 125.2(24)
(Si,Al)−O(1)−(Si,Al)	145.9(18)		
(Si,Al)−O(2)−(Si,Al)	127.5(13)	Zn(I′)−O(5)−Al(U)	99(3)
(Si,Al)−O(3)−(Si,Al)	121.5(15)	Zn(II′)−O(5)−Al(U)	123(3)
(Si,Al)−O(4)−(Si,Al)	142.9(16)		
		O(5)−Al(U)−O(5)	109(4)^c

^{a} Numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding parameter. ^{b} These distances are the longest in this group because the Zn^{2+} ions all coordinate to O(2) or O(3), never to O(1) or O(4). ^{c} All six angles are required to be tetrahedral by symmetry. The experimental esd of each angle is about 4°.

indicating that the sodalite units are not quite full with Zn$_7$HAlO$_4$$^{10+}$ ions.

Because the occupancy at Zn(II′) is only three-quarters that at Zn(I′), the structure determined does not have $\bar{4}3m$ symmetry about Wyckoff position 8(a) in the sodalite cavity. Numerous attempts to move Al(U) away from 8(a) and to differentiate two types of atoms at Zn(I′), as its large thermal parameters indicate (see Table 2), were unsuccessful with the present diffraction data. Similarly, O(5) could not be differentiated.

Fixed weights were used initially; the final weights were assigned using the formula $w = q/[\sigma^2(F_o^2) + (aP)^2 + bP + d + e \sin(\theta)]$, where $P = fF_o^2 + (1 − f)F_c^2$, to give $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$, with a and b as refined parameters (see Table 1). Atomic form factors for Si, Al, O, and Zn were used.[21] The form factor for (Si,Al) was that of Si diminished by a factor of 0.967 to give the correct number of electrons for a Si/Al framework ratio of 104/88 (vide infra). Final values and additional details are given in Table 1. The final structural parameters are presented in Table 2, and selected interatomic distances and angles are in Table 3.

Description of the Structure

(1) Description of Zeolite X. Zeolite X is a synthetic counterpart of the naturally occurring mineral faujasite (see Figure 1). The 14-hedron with 24 vertexes known as the sodalite cavity or β-cage may be viewed as its principal building block.

These β-cages are connected tetrahedrally at six-rings by bridging oxygens to give double six-rings (D6R's, hexagonal 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 (S6R's) are shared by sodalite and super-cages and may be viewed as the entrances to the sodalite units. Each unit cell has eight sodalite units, eight supercages, 16 D6R's, 16 12-rings, and 32 S6R's.

Exchangeable cations that 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 1: site I at the center of the D6R, I′ in the sodalite cavity on the opposite side of one of the D6R's six-rings from site I, II′ inside the sodalite cavity near a S6R, 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 or substantially away from III (off the 2-fold axis) on the inner surface of the supercage. Sometimes atoms or ions are found at the center of the sodalite unit, site U.[22]

(2) Zn$_{56}$Si$_{104}$Al$_{88}$O$_{384}$·8HAlO$_4$·8H. About 56 Zn^{2+} ions per unit cell are found at three crystallographic sites. Thirty nearly
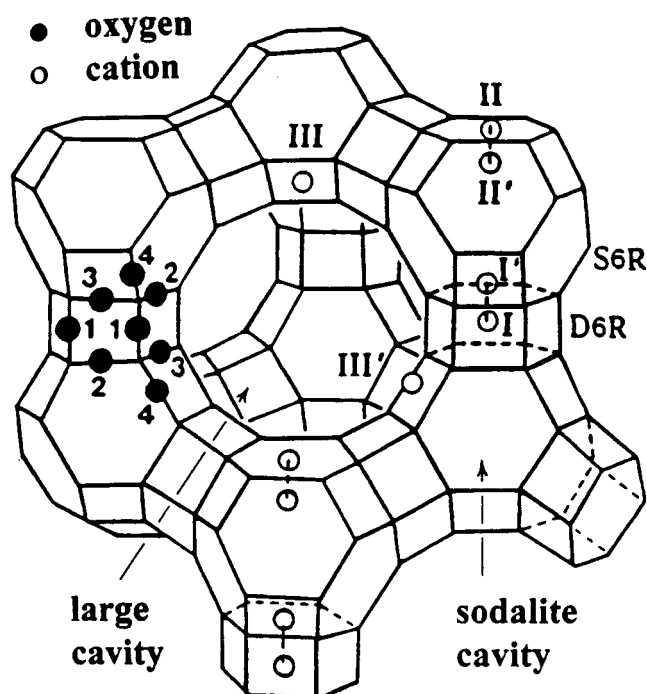
Figure 1. Stylized drawing of the framework structure of zeolite X. Near the center of the each line segment is an oxygen atom. The different oxygen atoms are indicated by the numbers 1−4. Silicon and aluminum atoms occupy the tetrahedral intersections without long-range order. Extraframework cation positions are labeled with Roman numerals. Site U at the center of the sodalite cavity is not shown.

fill site I′, 23 nearly three-quarters fill site II′, and the remaining three sparsely occupy site II (see Figure 2). Eight aluminate ions per unit cell fill the site U position at the centers of sodalite units. Sometimes, but not always, because there is a nonstoichiometric deficiency of Zn^{2+} ions and an excess of H^+ ions in the structures, three of the aluminate oxygens bridge between a site-I′ Zn^{2+} and a site-II′ Zn^{2+} ion; the remaining oxygen coordinates to only one site-I′ Zn^{2+} ion.

Why is the occupancy at site II′ only three-quarters that at site I′? Additional, although insufficient, Zn^{2+} ions that could occupy site II′ and coordinate to O(5) are readily available at site II. It is proposed that each aluminate ion has retained a proton, preventing Zn^{2+} ions from continuing to fill site II′. Three of the four aluminate oxygens are three-coordinate with Al^{3+} and two Zn^{2+}, while the fourth appears to be three-

coordinate with Al^{3+}, Zn^{2+}, and H^+. This H^+ ion can hydrogen bond weakly to an O(2) framework oxygen (O(5)−O(2) = 3.25 Å; Al(U)−O(5)−O(2) = 115°); see Figures 2 and 3. Additional available H^+ ions may allow other sodalite-unit aluminate ions to be $H_2AlO_4^{3-}$ coordinated perhaps to six Zn^{2+} ions.

Each Zn(I′) ion coordinates to three O(3)'s at 1.949(25) Å and to one aluminate oxygen, O(5), at 2.00(6) Å; each Zn(II′) coordinates to three O(2)'s at 2.019(22) Å and to one O(5) aluminate oxygen at 1.97(6) Å. This Zn(II′)−O(2) distance is the same as the 1.99(1)-Å distance found in zeolite A for three-coordinate six-ring Zn^{2+} ions;[14] both involve S6R's. For comparison, the sum of the ionic radii of Zn^{2+} and O^{2-} is 0.74 + 1.32 = 2.06 Å.[23a] The O(3)−Zn(I′)−O(3) and O(2)−Zn-(II′)−O(2) bond angles are 108.4(7)° and 112.5(7)°, respectively, nicely tetrahedral. The O(2 or 3)−Zn(I′ or II′)−O(5) angles are less regular; see Table 3. Each Zn(I′) ion extends 0.68 Å into the sodalite unit from its three-O(3) plane; each Zn(II′) ion extends 0.57 Å into the sodalite unit from its three-O(2) plane. See the stereoview given in Figure 4.

Each Zn(II) ion coordinates only to three O(2)'s at 2.00(3) Å, the same distance as Zn(II′), 2.019(22) Å. Each Zn(II) ion extends 0.51 Å into the supercage from its three-O(2) plane.

In the aluminate anion, the Al(U)−O(5) distances are 1.79(6) Å and the O(5)−Al(U)−O(5) bond angles are tetrahedral by symmetry (see Table 3).

The mean Zn^{2+}−O(2 or 3) distance, 1.99(3) Å, is much shorter than the corresponding mean distance, 2.21(2) Å, in Zn−Y,[19] consistent with the higher negative charge of the zeolite X framework. However, that Zn−Y work,[19] done by powder diffraction, may have failed to find sorbed Zn atoms; these atoms, by bonding to Zn^{2+}, could be responsible for the long 2.21(2) Å Zn−O mean distance.

Discussion

Complete Zn^{2+} exchange of a single crystal of Na_{92}-X was attempted from aqueous solution at 80 °C, followed by evacuation at 400 °C. Neither stoichiometric ion exchange nor simple dehydration to give empty Zn_{46}-X occurred. Instead, 55.0(15) Zn^{2+} ions and 7.9(7) nonframework aluminate ions were found.

It appears that the monomeric tetrahedral aluminate ion, AlO_4^{5-}, had not been seen before crystallographically until the powder diffraction work of Ciraolo et al. on Zn^{2+}-exchanged zeolite LSX.[20] It is seen more accurately in this work with a

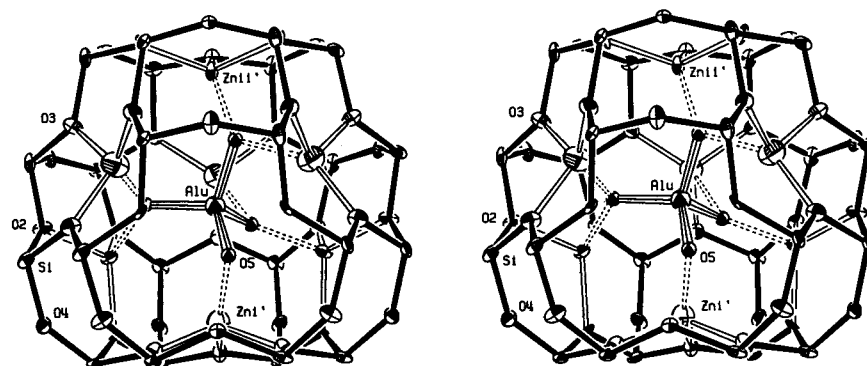**Figure 2.** Stereoview of a sodalite unit (black bonds) containing a tetrahedral aluminate ion, $(HAlO_4)^{4-}$ (striped bonds). The H atom bound to O(5) in the lower central foreground was not found crystallographically and is not shown. It can hydrogen bond weakly (O(5)−O(2) = 3.25 Å; Al(U)−O(5)−O(2) = 115°) to the O(2) oxygen to its right, somewhat above, in the front six-ring. Four Zn^{2+} ions at Zn(I′) lie at site I′ and three Zn^{2+} ions at Zn(II′) lie at site II′. Three of the four aluminate oxygens each bridge between a site-I′ Zn^{2+} and a site-II′ Zn^{2+} ion; the aluminate OH group coordinates only to a site-I′ Zn^{2+} cation. Broken bonds indicate aluminate coordination to Zn^{2+}, and white bonds indicate framework coordination to Zn^{2+}. Ellipsoids of 25% probability are used. For the purposes of these drawings, the thermal parameter U_{iso} for O(5) was increased by 1.0σ to a more reasonable value.
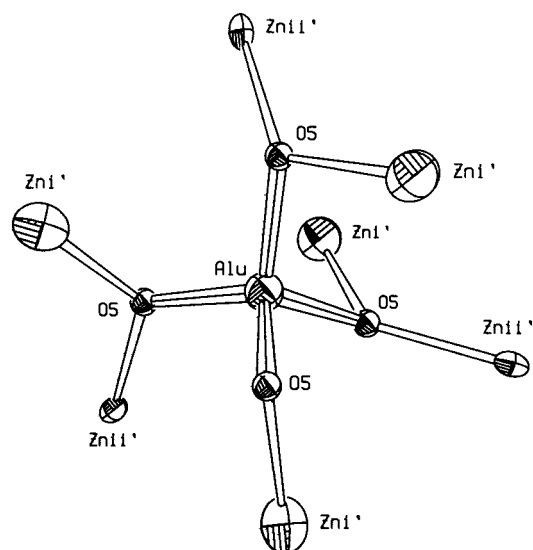
Figure 3. Aluminate anion coordinated by seven Zn^{2+} ions in a sodalite cavity: the $Zn_7HAlO_4{}^{10+}$ cluster. The O(5) atom in the foreground is presumed to be an OH group.

reliable oxygen position and Al–O bond length. The Al(U)–O(5) distance is the same as the 1.76 Å mean distance found in the tetrahedral aluminate dimer, $(HO)_3$–Al–O–Al–$(OH)_3{}^{2-}$;[24] for comparison, the sum of the ionic radii of four-coordinate Al^{3+} and three-coordinate O^{2-} is $0.39 + 1.36 = 1.75$.[23b] The $AlO_4{}^{5-}$ ion is stabilized by coordination to seven (sometimes six) Zn^{2+} ions and an H^+ ion (sometimes more), and the resulting clusters are stable within the sodalite cavity. The structure of the monomeric octahedral aluminate ion $Al(OH)_6{}^{3-}$ was recently determined crystallographically.[25]

To clarify whether the dealumination of the zeolite framework occurred during aqueous ion exchange at 80 °C or during subsequent vacuum dehydration as the temperature was raised to 400 °C, two additional crystals (fully hydrated Zn(II)-exchanged zeolite X and the same material partially dehydrated by evacuation at 23 °C) were prepared and their structures determined.[26] Neither crystal contained aluminate ions, and both crystals retained their long-range Si/Al ordering. It is therefore clear that the dealumination of the zeolite framework occurred during the high-temperature vacuum dehydration process; this was subsequently confirmed by solid-state NMR of LSX powder.[27] The number of Zn^{2+} ions were countable in the structure of the crystal evacuated at 23 °C; it had 54 Zn^{2+} ions per unit cell.

Both X-ray diffraction[28] and solid-state NMR[29–33] have been used to study the dealumination of zeolite Y. According to

powder diffraction studies on zeolite Y dealuminated by chemical extraction, the vacancies at aluminum sites in the framework are replaced by silicon atoms migrating from the crystallite surface or from amorphous material that may have been present. No structural defects were noted in the diffraction pattern and the unit-cell constant had decreased, indicating that recrystallization had occurred to give an increased Si/Al ratio.[28] Solid-state NMR studies on NH₄,Na-Y revealed that dealumination occurred upon dehydration at high temperature,[29–33] as is seen in this work. As the temperature increased, the degree of dealumination increased and the framework Si/Al ratio increased without change in overall chemical composition. The intensities of the Si(3Al) and Si(2Al) signals sharply decreased, while that of Si(0Al) increased correspondingly. This proved that the vacancies were replaced by silicon atoms from elsewhere in the crystal, maintaining the integrity (full occupancy) of the dealuminated zeolite framework.[29–33]

Therefore, in this work, the zeolite framework should retain its $(Si,Al)_{192}O_{384}{}^{n-}$ stoichiometry. This is in fact indicated by the continued ability of the crystal to give sharp diffraction peaks. However, the number of Si and Al atoms per unit cell has increased from $100 + 92 = 192$ before high-temperature dehydration to $192 + 7.9 (7) = 200$ afterward. Because there is no other source of Si or Al atoms than the crystal itself, a decrease in the number of unit cells to about 192/200 of its initial value is indicated. Concomitantly, the Zn^{2+} ions should have been concentrated in the surviving unit cells, increasing from 54 to about $(200/192)(54) = 56.3$ per unit cell; this can be compared to the value found in this work, 55.0(15); 56 is the convenient integer selected for this value in the discussion to follow. In addition, the number of Si atoms per unit cell should have increased from 100 to about $(200/192)(100) = 104.2$, assuming no loss of Si from the zeolite framework. Complimentarily the number of Al atoms per unit cell in the zeolite framework should have decreased from 92 to about $192 - 104.2 = 87.8$; 104 and 88 are the corresponding integers selected for the discussion to follow.

In accordance with above argument, the framework should have composition $Si_{104}Al_{88}O_{384}$; the total negative charge with eight $AlO_4{}^{5-}$ ions is $-88 + 8 \times (-5) = -128$. Including the 56 Zn^{2+} ions per unit cell gives $Zn_{56}Si_{104}Al_{88}O_{384} \cdot 8AlO_4$ with a total charge of $56 \times (+2) + (-128) = -16$ per unit cell. The 16 positive charges needed to compensate this negative charge are likely to be from H^+ ions not located crystallographically. These could be the result of the reaction of released $AlO_2{}^-$ with H_2O, and they could remain associated with $AlO_4{}^{5-}$ or dissociate to interact with framework oxygens. The Zn^{2+} occupancy at site II′ indicates that at least eight H^+ ions per
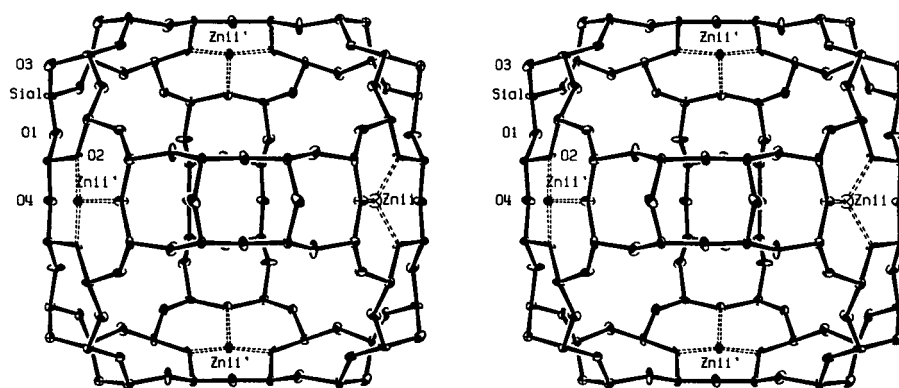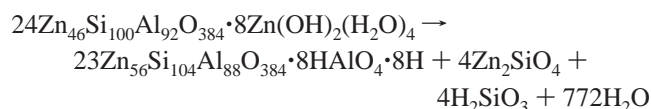

Figure 4. Stereoview of perhaps half of the supercages showing three Zn(II′) and one Zn(II) ion. The remainder would have only three Zn(II′) ions.

unit cell remain with aluminate ions to form clusters of Zn_7HAlO_4. However, both stoichiometry and crystallography indicate that there are not enough Zn^{2+} ions per unit cell for Zn_7HAlO_4 to be present in all sodalite units, so some aluminate is likely to be $H_2AlO_4^{3-}$ coordinated by fewer than seven Zn^{2+} ions. As a result of these H^+ ions, some Zn^{2+} ions are excluded from the sodalite unit. With uncertainty regarding the positions of the final eight H^+ ions, the composition of the unit cell is written as $Zn_{56}Si_{104}Al_{88}O_{384}\cdot 8HAlO_4\cdot 8H$.

The above formula indicates that four aluminum atoms per unit cell have been replaced by silicon. A source is needed for these four silicon atoms and for the four additional aluminum atoms needed to give the eight aluminate ions per unit cell. Therefore, both silicate and aluminate must have migrated from other (dissolving) unit cells to each remaining (surviving) unit cell. As a result of this self-recrystallization process, the zeolite framework becomes enriched in silicon. Zn^{2+} ions can also migrate from the disappearing unit cells to the surviving ones; the number of Zn^{2+} ions per unit cell may have increased during the dehydration process.

The overall process, loss of some aluminum from the zeolite framework to the sodalite-cavity centers, migration of silicon and aluminum within the framework, and the concentration of Zn^{2+} ions in the surviving unit cells, may be written as the following net reaction, which assumes that no aluminum leaves the crystal. It describes the condensation of 24 unit cells to give 23 unit cells and may be incorrect in its details:

$$24Zn_{46}Si_{100}Al_{92}O_{384}\cdot 8Zn(OH)_2(H_2O)_4 \rightarrow$$
$$23Zn_{56}Si_{104}Al_{88}O_{384}\cdot 8HAlO_4\cdot 8H + 4Zn_2SiO_4 +$$
$$4H_2SiO_3 + 772H_2O$$

The minor amounts of silicate products should not be fully hydrous because they have been evacuated at 400 °C. They could be absent if the Si/Al ratio of the zeolite studied was 1.00. They could have migrated to the crystal surface during the dehydration process; this would explain the white appearance of the crystal studied.

The relatively small diffraction data set and relatively high error indices (see Table 1) indicate that the crystal retains enough imperfections to be considered damaged.

Summary

Aqueous Zn^{2+} exchange of Na-X at 80 °C resulted in over-exchange due formally to the uptake of $Zn(OH)_2$. Evacuation as the temperature was increased to 400 °C caused the zeolite framework to lose aluminate and to reconstruct itself to become enriched in silicon. In addition, the zeolite has lost its long-range Si/Al ordering, leading to the change of space group from $Fd\bar{3}$ to $Fd\bar{3}m$. Some, perhaps all, of the aluminate lost by the framework has been retained to fill sodalite cavities with Zn_7-$HAlO_4^{10+}$ and similar clusters somewhat poorer in Zn^{2+} and richer in H^+.

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