

Chemistry and Crystallographic Studies of Metal Ion Exchanged Zeolite X.

I. The Crystal Structure of Fully Dehydrated and Fully K^+ -Exchanged Zeolite X, $K_{92}X$

Se Bok Jang and Yang Kim*

Department of Chemistry, Pusan National University, Pusan 609-735, Korea

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The crystal structure of $K_{92}X$ ($K_{92}Al_{92}Si_{100}O_{384}$), $a = 25.128(1)$ Å, dehydrated at 360°C and 2×10^{-6} Torr, has been determined by single-crystal X-ray diffraction techniques in the cubic space group $Fd\bar{3}$ at $21(1)$ °C. The structure was refined to the final error indices $R_1 = 0.044$ and $R_w = 0.039$ with 242 reflections for which $I > 3\sigma(I)$. In this structure, ninety-two K^+ ions are located at the five different crystallographic sites. Sixteen K^+ ions are located at the centers of the double six rings (site I; $K(1)-O(3) = 2.65(2)$ Å and $O(3)-K(1)-O(3) = 92.0(6)^\circ$). About twelve K^+ ions lie at site I' in the sodalite cavity opposite double six rings (D6R's) and these K^+ ions are recessed *ca.* 1.62 Å into the sodalite cavity from their O(3) plane ($K(2)-O(3) = 2.74(2)$ Å, $O(3)-K(2)-O(3) = 88.5(8)^\circ$). About thirty-two K^+ ions are located at the site II in the supercage and these K^+ ions are recessed *ca.* 1.20 Å into the supercage from their O(2) plane ($K(3)-O(2) = 2.64(2)$ Å, and $O(2)-K(3)-O(2) = 101(1)^\circ$). About twenty-two K^+ ions lie at the site III in the supercage opposite 4-ring ladder and the remaining ten K^+ ions lie at the site III' near the 4-ring ladder in the supercage ($K(4)-O(4) = 2.88(3)$ Å, $O(4)-K(4)-O(4) = 79.8(9)^\circ$, $K(5)-O(4) = 2.8(2)$ Å, and $O(4)-K(5)-O(4) = 68(5)^\circ$).

Introduction

Zeolite X has a framework with a structure similar to that of the natural mineral faujasite. The chemical composition can vary according to the silicon and aluminium content from a Si/Al ratio ≈ 1.0 -1.5. The increase in the aluminium content leads to the increase of the number of exchangeable cations and affects their distribution in the different possible sites in the framework cavities. Zeolite X has a wide range of industrial application primarily due to the excellent stability of the crystal structure and a large available pore volume and surface area.¹ In addition to the accessible pore volume, the adsorptive and catalytic properties of zeolites heavily depend on the size, charge density, and distribution of cations in the lattice.

Because of their importance in adsorption and catalysis, zeolites have been the subject of numerous investigation. Alkali-metal cation exchanged zeolites are of interest for use in catalysis and sorption. Li-exchanged zeolites X and Y were studied using powder² and single crystal diffraction data.³ Smith *et al.* investigated a single-crystal of a dehydrated K^+ -exchanged natural faujasite (Si/Al = 2.3).⁴ The structures of four hydrated⁵ and dehydrated⁶ partially K^+ -exchanged X and Y zeolites with various Si/Al ratios were also studied using X-ray powder data.

Recently, single crystals of $K_{92}X \cdot 50K^7$ and $Cs_{92}X \cdot 36Cs^8$ were synthesized by exposing Na-X to the corresponding alkali metal vapor, and their structures were determined by X-ray diffraction methods. At high potassium loadings, all potassium clusters in the sodalite cavities of zeolite X were linked by potassiums at the centers of double six-oxygen rings (D6R's) to form rings or chains (one-dimensional continua: zig-zag strands). In $Cs_{92}X \cdot 36Cs$, all sodalite and supercage cavities are "full" of cesiums in this structure. Each sodalite cavity contains two cesiums which attach as a linear

appendix, one per supercage. A three-dimensional potassium continuum, similar to that found in $Cs_{92}X \cdot 36Cs$, formed in $K_{92}X \cdot 50K$.⁷ A cationic cesium continuum was found to be present in $Cs_{92}X \cdot 36Cs$.⁸ This superlattice cluster fills all of the channels and cavities of the zeolite framework to form an interpenetrating structure. Pseudo-icosahedral clusters, each with a cesium atom at its center, in the supercages of zeolite X are arranged as the carbon atoms in diamond, tetrahedrally connected to form the continuum.

Up to this time, no structural study of the dehydrated fully K^+ -exchanged zeolite X has been reported. This work was initiated to investigate the selective positions and the bonding characteristics of K^+ ions in the crystal structure of the dehydrated fully K^+ -exchange zeolite X.

Experimental Section

Large single crystals of sodium zeolite X, stoichiometry $Na_{92}Al_{92}Si_{100}O_{384}$, were prepared in St. Petersburg, Russia.⁹ One of these, a colorless octahedron about 0.20 mm in cross-section was lodged in a fine Pyrex capillary.

To prepare fully K^+ -exchanged zeolite X, an exchange solution of KNO_3 and KOH in the molar ratio of 1:1 with total concentration of 0.05 M was used. Ion exchange was accomplished by flow methods; the solution was allowed to flow past the crystal at a velocity of approximately 1.5 cm/s for 5 days at $24(1)$ °C. The clear, colorless, hydrated K^+ -exchanged X was dehydrated at 360°C and 2×10^{-6} Torr for 2 days.

After cooling to room temperature, the crystal, still under vacuum, was sealed in its capillary by torch. Microscopic examination showed that the crystal has become red.

The cubic space group $Fd\bar{3}$ was used throughout this work. Diffraction data were collected with an automated Enraf-Nonius four-circle computer controlled CAD-4 diffractometer

equipped with a pulse-height analyzer and a graphite monochromator, using Mo K α radiation ($K_{\alpha 1}$, $\lambda=0.70930$ Å, $K_{\alpha 2}$, $\lambda=0.71359$ Å). The unit cell constants at 21(1) °C determined by least-squares refinement of 25 intense reflections for which $14^\circ < 2\theta < 24^\circ$ are $a=25.128(1)$ Å for dehydrated K $_{92}$ -X.

The ω -2 θ scan technique was used. The data were collected using variable scan speeds. Most reflections were observed at slow scan speeds, ranging between 0.23 and 0.32 deg min $^{-1}$ in ω . The intensities of three reflections in diverse regions of reciprocal space were recorded after every three hours to monitor crystal and X-ray source stability. Only small random fluctuations of these check reflections were noted during the course of data collection. The intensities of all lattice points for which $2\theta < 60^\circ$ were recorded.

Of the 1205 reflections examined, only the 242 whose net counts exceeded three times their corresponding esd's were used in structure solution and refinement.

The intensities were corrected for Lorentz and polarization effects; the reduced intensities were merged and the resultant estimated standard deviations were assigned to each reflection by the computer programs, GENESIS, PROCESS and WEIGHT.¹⁰

An absorption correction ($\mu R=0.101$,¹¹ $\rho_{\text{calc}}=1.574$ g/cm 3 and $F(000)=7370$) was made empirically using a ψ scan. The calculated transmission coefficients ranged from 0.965 to 0.998. This correction had little effect on the final R indices.

Structure Determination

Full-matrix least-squares refinement was initiated with atomic thermal parameters of the framework atoms [Si, Al, O(1), O(2), O(3) and O(4)] in dehydrated Ca $_{32}$ K $_{28}$ -X.¹² Anisotropic refinement of the framework atoms converged to an R_1 index, $(\sum |F_o - |F_c||/F_o)$ of 0.28 and a weighted R_2 index, $(\sum_w (F_o - |F_c|)^2 / \sum_w F_o^2)^{1/2}$ of 0.32.

A difference Fourier function revealed two large peaks at (0.0, 0.0, 0.0) and (0.241, 0.241, 0.241) with heights of 11.2

and 7.96 eÅ $^{-3}$, respectively. These two peaks were stable in least-squares refinement. Isotropic refinement including these K $^+$ ions at K(1) and K(3) positions converged to $R_1=0.120$ and $R_2=0.142$ with occupancies of 15.3(5) and 29.9(6), respectively (see Table 1).

A subsequent difference Fourier synthesis showed the positions of K $^+$ ions at K(4), (0.412, 0.125, 0.125), with peak height 4.22 eÅ $^{-3}$ and K $^+$ ions at K(2), (0.069, 0.069, 0.069), with peak height 3.66 eÅ $^{-3}$. These were stable in least-squares refinement, and anisotropic refinement of framework atoms and isotropic refinement of K(4) and K(2) converged to $R_1=0.045$ and $R_2=0.043$ with occupancies of 21.2(10) and 8.6(18), respectively.

From successive difference Fouriers, one peak was found at (0.42, 0.06, 0.05), height=2.44 eÅ $^{-3}$, which refined as K(5). Simultaneous positional and isotropic thermal parameter refinement with varied occupancy numbers converged to the error indices $R_1=0.042$ and $R_2=0.037$. The occupancy numbers of K(1), K(2), K(3), K(4) and K(5) per unit cell were refined to 15.3(5), 12.5(8), 29.9(7), 21.2(10), and 8.6(18), respectively. These were fixed at 16.0, 12.0, 32.0, 22.0 and 10.0, respectively, because the cationic charge should not be exceeded +92 per $Fd\bar{3}$ unit cell as in the last column of Table 1.

All shifts in the final cycles of least-squares refinement were less than 0.1% of their corresponding standard deviations. The final error indices converged to $R_1=0.044$ and $R_2=0.039$. The final difference function was featureless except for a peak at (0.277, 0.973, 0.777) of height 0.74 eÅ $^{-3}$. This peak was not within bonding distance of any other atom, and was not considered further.

All crystallographic calculations were done using the MOIEN (a structure determination package programs, supplied by Enraf-Nonius).¹⁰ The full-matrix least-squares program used minimized $\sum w(F_o - |F_c|)^2$; the weight (w) of an observation was the reciprocal square of $\sigma(F_o)$, its standard deviation. Atomic scattering factors^{13,14} for Si, Al, O $^-$, and K $^+$ were used. All scattering factors were modified to account for

Table 1. Positional, Thermal, and Occupancy Parameters for Dehydrated K $_{92}$ -X

Atom	Wyc. Pos.	x	y	z	$^a\beta_{11}$, B_{110}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy varied	Fixed
Si	96(g)	-553(3)	349(3)	1240(5)	5(1)	4(1)	4(1)	2(3)	2(4)	2(4)		96
Al	96(g)	-555(3)	1244(5)	354(3)	3(1)	4(1)	2(1)	0(4)	-1(2)	-3(4)		96
O(1)	96(g)	-1090(8)	-10(10)	1100(8)	8(4)	16(4)	6(4)	-5(8)	-0(5)	-7(7)		96
O(2)	96(g)	-38(8)	-43(9)	1394(6)	4(3)	8(4)	6(4)	4(6)	-4(7)	0(7)		96
O(3)	96(g)	-376(7)	693(9)	703(9)	12(4)	9(4)	11(4)	-14(8)	2(9)	18(6)		96
O(4)	96(g)	-679(7)	726(9)	1765(9)	5(4)	13(4)	9(4)	0(9)	0(8)	-14(6)		96
K(1)	16(c)	0	0	0	18(2)	18(2)	18(2)	28(4)	28(4)	28(4)	15.3(5)	16
K(2)	32(e)	710(10)	710(10)	710(10)	15(4)	15(4)	15(4)	3(9)	3(9)	3(9)	12.5(8)	12
K(3)	32(e)	2435(3)	2435(3)	2435(3)	11(1)	11(1)	11(1)	12(3)	12(3)	12(3)	29.9(7)	32
K(4)	48(f)	4060(10)	1250	1250	7(5)	30(7)	39(8)	0	0	-30(10)	21.2(10)	22
K(5)	96(g)	4270(70)	680(80)	560(80)	18(6) ^d						8.6(18)	10

^aPositional and anisotropic thermal parameters are given $\times 10^4$. Numbers in parentheses are the esd's in the units of the least significant digit given for the corresponding parameter. ^bThe anisotropic temperature factor = $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. ^cOccupancy factors are given as the number of atoms or ions per unit cell. ^dIsotropic thermal parameter in units of Å 2 .

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

Si-O(1)	1.65(2)
Si-O(2)	1.67(2)
Si-O(3)	1.66(2)
Si-O(4)	1.65(2)
Al-O(1)	1.67(2)
Al-O(2)	1.66(2)
Al-O(3)	1.70(2)
Al-O(4)	1.67(3)
K(1)-O(3)	2.65(2)
K(2)-O(3)	2.74(2)
K(3)-O(2)	2.64(2)
K(4)-O(1)	3.39(3)
K(4)-O(4)	2.88(3)
K(5)-O(1)	3.2(2)
K(5)-O(4)	2.8(2)
K(1)-K(2)	3.10(1)
O(1)-Si-O(2)	111(1)
O(1)-Si-O(3)	109(1)
O(1)-Si-O(4)	109(1)
O(2)-Si-O(3)	107(1)
O(2)-Si-O(4)	108(1)
O(3)-Si-O(4)	114(1)
O(1)-Al-O(2)	112(1)
O(1)-Al-O(3)	107(1)
O(1)-Al-O(4)	109(1)
O(2)-Al-O(3)	107(1)
O(2)-Al-O(4)	108(1)
O(3)-Al-O(4)	114(1)
Si-O(1)-Al	130(1)
Si-O(2)-Al	150(1)
Si-O(3)-Al	140(1)
Si-O(4)-Al	151(1)
O(3)-K(1)-O(3)	92.0(6)
O(3)-K(2)-O(3)	88.5(8)
O(2)-K(3)-O(2)	101(1)
O(1)-K(4)-O(1)	139.4(9)
O(4)-K(4)-O(4)	79.0(9)
O(1)-K(5)-O(1)	110(6)
O(4)-K(5)-O(4)	68(5)

Numbers in parentheses are estimated standard deviations in the least significant digit given for the corresponding value.

anomalous dispersion.¹⁵ The final structural parameters and selected interatomic distances and angles are presented in Tables 1 and 2, respectively.

Discussion

In this crystal structure, 92 K^+ ions are located at the five different crystallographic sites. Sixteen K^+ ions at K(1) lie at site I in the center of a double six-oxygen ring (D6R). This 16-fold position is fully occupied. Each K^+ ion at K(1) is coordinated by six O(3) oxygen atoms of hexagonal prism at distance of 2.65 Å, which is the same distance as the

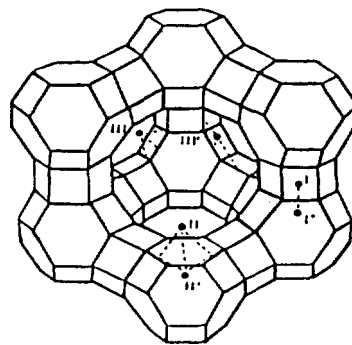


Figure 1. Framework structure of zeolite X. Extraframework cation positions are labeled with Roman numerals.

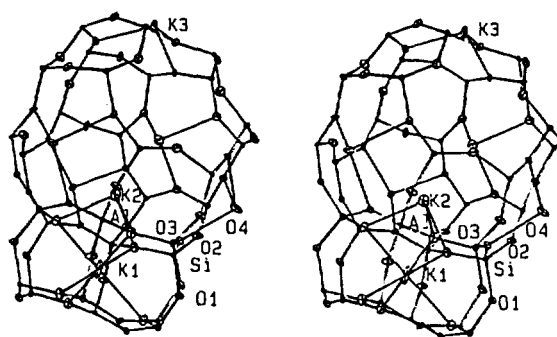


Figure 2. A stereoview of sodalite cavity of dehydrated $K_{92}X$. One K^+ ion at K(1) lies at site I, the center of the double six ring and four K^+ ions at K(3) lie at site II. All double six rings have this arrangement. In about 50% of the sodalite cavities, two K^+ ions at K(2) lie at site I' and in the remaining 50% of sodalite cavities, only one K^+ ions at K(2) lies at site I'. Ellipsoids of 20% probability are shown.

sum of the ionic radii of K^+ and O^{2-} , $1.33 + 1.32 = 2.65$ Å.¹⁶ The K^+ ions at K(2) are located at site I' in the sodalite cavity opposite double six rings (D6R's). Each K^+ ion at K(2) is recessed *ca.* 1.62(1) Å into the sodalite cavity from its 6-ring plane. Twelve out of 32 positions are occupied and sixteen site I's are fully occupied by K^+ ions at K(1) (see Figures 1 and 2). Therefore each twelve K^+ ions at K(2) must have an adjacent K^+ ion at K(1) at 3.10(1) Å. Because of intercationic repulsion, K^+ ion at K(2) is rather far from framework oxygens (K(2)-O(3)=2.74(2) Å).

The extra-framework cations that compensate for the negative charge of the framework occupy the various positions, called the sites I, I', II, II', III, and III' (see Figure 1).^{4,8} The site I is in the center of hexagonal prism. The site II is in the supercage adjacent to the single six-membered ring. The site I' and II' lie on the opposite sides of the six-membered ring in sodalite cavities as compared with the sites I and II. The site III lies in supercages opposite 4-ring and the site III' lies at a little bit off the site III.

Thirty-two K^+ ions at K(3) lie at site II and are recessed 1.20 Å into the supercage from the single 6-ring plane at O(2). This 32-fold position is also fully occupied, or nearly so. The K(3)-O(2) distance, 2.64(2) Å agrees well with the sum of K^+ and O^{2-} radii, 2.65 Å. The angle subtended at

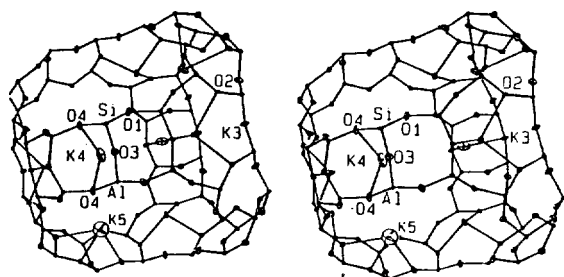


Figure 3. A stereoview of large cavity of dehydrated K_{92} -X. Four K^+ ions at K(3) lie at site II, three K^+ ions at K(4) lie at site III and one K^+ ion at K(5) lies at site III'. About 75% of the large cavities may have this arrangement. Remaining about 25% may have four K^+ ions at K(3), two K^+ ions at K(4), and two K^+ ion at K(5). Ellipsoids of 20% probability are shown.

$K(3)$, $O(2)$ - $K(3)$ - $O(2)$ is $101(1)^\circ$.

Twenty-two K^+ ions at K(4) lie in the supercage at site III. This is 48-fold position, but this is occupied by only 22 K^+ ions (Figure 3). The K^+ ions at K(4) are loosely held to framework oxygens $K(4)$ - $O(1)=3.39(3)$ Å and $K(4)$ - $O(4)=2.88(3)$ Å. Ten K^+ ions at K(5) lie in the supercage at site III'. This is 96-fold position, but this is occupied by only 10 K^+ ions (Figure 3). The K^+ ions at K(4) are also loosely held to framework oxygens $K(4)$ - $O(1)=3.2(2)$ Å and $K(4)$ - $O(4)=2.8(3)$ Å. These distances are substantially longer than the sum of the ionic radii. Such long interaction distances have been observed previously in supercage (and/or large cavity) in other X and A structures.^{7,17,18}

Recently the crystal structure of dehydrated Ca^{2+} and K^+ -exchanged zeolite X, $Ca_{32}K_{28}$ -X, has been determined by single-crystal X-ray diffraction methods.¹² In this structure, all Ca^{2+} ions and K^+ ions occupy four different crystallographic sites; sixteen Ca^{2+} ions at site I, the centers of the double six-oxygen rings (symmetry of 3), sixteen Ca^{2+} ions and sixteen K^+ ions are located two different sites II in the supercage opposite 6-oxygen ring (symmetry of 3). These Ca^{2+} ions and K^+ ions are recessed 0.56 Å and 1.54 Å, respectively, into the supercage from their $O(2)$ oxygen planes. Twelve K^+ ions lie at the site III at the twofold axis of the edge of the four ring ladders inside supercage. Because the ionic radius of K^+ ion is larger than that of Ca^{2+} ion, large K^+ ions preferentially occupy at sites II and III deep in the large supercage. Smaller Ca^{2+} ions occupy smaller pore sites such as the centers of the double 6-rings and the positions near the centers of single 6-ring planes in the supercage.

Shepelev, Butikova and Smolin¹⁷ studied the crystal structures of the hydrated and dehydrated (400 °C) partially K^+ -, Rb^+ -, and Cs^+ -exchanged zeolite X. They investigated the migration of cations during the dehydration. Analysis of the cation distribution in the hydrated forms shows that K^+ ions penetrate into all zeolite cavities, whereas Rb^+ ions diffuse

into the sodalite cage, but not into the hexagonal prism, and Cs^+ ions are located only in the supercage. Dehydration of the zeolites is accompanied by a migration of unexchanged sodium cations into the hexagonal prism. Destruction of the dehydrated Rb^+ -exchanged crystal after the 6 hour-long exposure at 400 °C seems to be caused by a slow migration of the Rb^+ ions into the hexagonal prism. They located Na^+ ions at sites I, I', and II and K^+ ions at sites I', II, II', III and III' in the structure of dehydrated partially K^+ -exchanged zeolite X.

In this work, fully K^+ -exchanged zeolite X was successfully synthesized and its structure was determined by X-ray diffraction methods. Ninety-two K^+ ions are distributed in the sites I, I', II, III and III' (see Figure 1, 2 and 3).

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