

Crystal Structures of Zeolite X Exchanged by Two Different Cations. Structures of $\text{Cd}_{32}\text{Cs}_{28}\text{-X}$ and $\text{Cd}_{28}\text{Rb}_{36}\text{-X}$ ($\text{X} = \text{Si}_{100}\text{Al}_{92}\text{O}_{384}$)

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Two anhydrous crystal structures of fully dehydrated Cd^{2+} - and Cs^+ -exchanged zeolite X, $\text{Cd}_{32}\text{Cs}_{28}\text{Si}_{100}\text{Al}_{92}\text{O}_{384}$ ($\text{Cd}_{32}\text{Cs}_{28}\text{-X}$; $a = 24.828(11)$ Å) and fully dehydrated Cd^{2+} - and Rb^+ -exchanged zeolite X, $\text{Cd}_{28}\text{Rb}_{36}\text{Si}_{100}\text{Al}_{92}\text{O}_{384}$ ($\text{Cd}_{28}\text{Rb}_{36}\text{-X}$; $a = 24.794(2)$ Å), have been determined by single-crystal X-ray diffraction techniques in the cubic space group $Fd\bar{3}$ at 21(1)°C. The structures were refined to the final error indices, $R_1 = 0.058$ and $R_2 = 0.065$ with 637 reflections for $\text{Cd}_{32}\text{Cs}_{28}\text{-X}$ and $R_1 = 0.086$ and $R_2 = 0.113$ with 521 reflections for $\text{Cd}_{28}\text{Rb}_{36}\text{-X}$ for which $I > 3\sigma(I)$. In the structure of $\text{Cd}_{32}\text{Cs}_{28}\text{-X}$, 16 Cd^{2+} ions fill the octahedral sites I at the centers of the double six rings ($\text{Cd-O} = 2.358(8)$ Å and $\text{O-Cd-O} = 90.8(3)^\circ$). The remaining 16 Cd^{2+} ions occupy site II ($\text{Cd-O} = 2.194(8)$ Å and $\text{O-Cd-O} = 119.7(4)^\circ$) and six Cs^+ ions occupy site II opposite to the single six-rings in the supercage; each is 2.322 Å from the plane of three oxygens ($\text{Cs-O} = 3.193(13)$ and $\text{O-Cs-O} = 73.0(2)^\circ$). About ten Cs^+ ions are found at site II', 1.974 Å into the sodalite cavity from their three oxygen plane ($\text{Cs-O} = 2.947(8)$ Å and $\text{O-Cs-O} = 80.2(3)^\circ$). The remaining 12 Cs^+ ions are distributed over site III' ($\text{Cs-O} = 3.143(9)$ and $\text{O-Cs-O} = 59.1(2)^\circ$). In the structure of $\text{Cd}_{28}\text{Rb}_{36}\text{-X}$, 16 Cd^{2+} ions fill the octahedral sites I at the center of the double-six rings ($\text{Cd-O} = 2.349(15)$ and $\text{O-Cd-O} = 91.3(5)^\circ$). Another 12 Cd^{2+} ions occupy two different II sites ($\text{Cd-O} = 2.171(18)/2.269(17)$ Å and $\text{O-Cd-O} = 119.7(7)/113.2(7)^\circ$). Fifteen Rb^+ ions occupy site II ($\text{Rb-O} = 2.707(17)$ Å and $\text{O-Rb-O} = 87.8(5)^\circ$). The remaining 21 Rb^+ ions are distributed over site III' ($\text{Rb-O} = 3.001(16)$ Å and $\text{O-Rb-O} = 60.7(4)^\circ$). It appears that the smaller and more highly charged Cd^{2+} ions prefer sites I and II in that order, and the larger Rb^+ and Cs^+ ions, which are less able to balance the anionic charge of the zeolite framework, occupy sites II and II' with the remainder going to the least suitable site in the structure, site III'. The maximum Cs^+ and Rb^+ ion exchanges were 30% and 39%, respectively. Because these cations are too large to enter the small cavities and their charge distributions may be unfavorable, cation-sieve effects might appear.

Key words : Structure, Zeolite-X, Cadmium, Rubidium, Cesium

Introduction

The crystal structure of zeolite X in its hydrated form was determined by Broussard and Shoemaker¹ using powder diffraction techniques. The crystal structure of hydrated Na-X has been reinvestigated using single crystal X-ray techniques.²

The exchangeable cations in zeolites have received a great deal of attention in the scientific literature. The thermal stability, sorption parameters, and catalytic properties of zeolites are all determined by the type and number of exchangeable cations and their distribution over the available sites. Cation distributions in faujasite-type zeolites have been widely studied by X-ray diffraction methods.³⁻⁵

Calligaris *et al.* studied the crystal structures of hydrated ($\text{Cd}_{41}\text{Si}_{104}\text{Al}_{88}\text{O}_{384} \cdot 233\text{H}_2\text{O}$) and partially dehydrated Cd^{2+} -exchanged zeolite X ($\text{Cd}_{41}\text{Si}_{104}\text{Al}_{88}\text{O}_{384} \cdot 138\text{H}_2\text{O}$).⁶ The positions and occupancy number of Cd^{2+} ions and H_2O molecules in hydrated $\text{Cd}_{41}\text{-X}$ were then compared with those of partially hydrated $\text{Cd}_{41}\text{-X}$. Partial dehydration caused the movement of some cations from sites I' and III' to

I and II. The coordination number of the Cd^{2+} ions generally decreased, and the water molecules lost were primarily from the supercage.

Shepelev, Butikova, and Smolin studied the crystal structures of the partially K^+ -, Rb^+ -, and Cs^+ -exchanged forms of NaX zeolite in both the hydrated and the dehydrated (400 °C) states.⁷ They investigated the migration of cations during 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 and Cs^+ ions are located in the supercage. Dehydration of the zeolites is accompanied by the migration of unexchanged sodium cations into the hexagonal prism. Destruction of the dehydrated Rb^+ -exchanged crystal after the 6 h exposure at 400 °C seems to be caused by a slow migration of the Rb^+ ions into the hexagonal prism.⁷

In our recent work, the crystal structures of $\text{Ca}_{32}\text{K}_{28}\text{-X}$,⁸ $\text{Ca}_{31}\text{Rb}_{30}\text{-X}$,⁹ $\text{Cd}_{24.5}\text{Tl}_{43}\text{-X}$,¹⁰ $\text{Sr}_{31}\text{K}_{30}\text{-X}$, and $\text{Sr}_{8.5}\text{K}_{7.5}\text{-X}$,¹¹ have been determined. In these structures, the smaller and more highly charged Cd^{2+} , Ca^{2+} , and Sr^{2+} ions occupy site I, the center of a hexagonal prism, with the remainder going to site II. The larger Rb^+ and K^+ ions, which are less able to balance the anionic charge of the zeolite framework because

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of their size, finish satisfying the double six ring with some occupancy at sites, 1' and 11, with the remainder going to sites 111 and 111', the least suitable cation site in the structure.

In this work, the occupancy number and locations of cations in the structure of dehydrated $\text{Cd}_{32}\text{Cs}_{28}\text{-X}$ are compared with those of dehydrated $\text{Cd}_{28}\text{Rb}_{36}\text{-X}$. This study was performed to learn the selective positions of Cd^{2+} and Cs^- (or Rb^-) ions within zeolite X and to investigate accurately the geometry of Cs^+ (or Rb^-) and Cd^{2+} ions because of the large difference in their atomic scattering factors and ionic radii.¹²

Experimental Section

Large single crystals of zeolite Na-X with the stoichiometry of $\text{Na}_{92}\text{Si}_{100}\text{Al}_{20}\text{O}_{384}$ were prepared in St. Petersburg, Russia.¹³ One of these, a colorless octahedron about 0.2 mm in cross-section, was lodged in a fine Pyrex capillary.

An exchanged solution of $\text{Cd}(\text{NO}_3)_2$ and $\text{Cd}(\text{O}_2\text{CCH}_3)_2$ in the mole ratio of 1 : 1 with a total concentration of 0.05 M, was allowed to flow past the crystal for 5 days. This crystal was successively exchanged using a 0.05 M CsNO_3 solution for 3 days. Similarly, $\text{Cd}_{28}\text{Rb}_{36}\text{-X}$ was prepared by the flow method using an exchange solution whose $\text{RbOH} : \text{RbNO}_3$ mole was 1 : 10 with a total concentration of 0.05 M for 3 days. The capillaries containing the crystals were attached to a vacuum system, and these crystals were cautiously dehydrated by gradually increasing the temperature (ca. 29 °C/h) to 450 °C at a constant pressure of 2×10^{-6} Torr. Finally, the system was maintained at this state for 2 days and both crystals, which were colorless initially, became dark blue. After cooling to room temperature, each crystal, still under vacuum, was sealed in its capillary by touch.

The cubic space group $Fd\bar{3}$ was used throughout this work. This choice is supported by (a) the low Si/Al ratio which in turn requires, at least in the short range, the alternation of Si and Al, and (b) the observation that this crystal, like all other crystals from the same batch, does not have intensity symmetry across (110) and therefore lacks that mirror plane. Diffraction data were collected with an automated Enraf-Nonius four-circle computer-controlled CAD-4 diffractometer equipped with a pulse-height analyzer and graphite monochromator, using Mo radiation ($K\alpha_1$, $\lambda = 0.70930$; $K\alpha_2$, $\lambda = 0.71359$ Å). The cubic unit cell constant at 21(1) °C, determined by least-squares refinement of 25 intense reflections for which $14^\circ < 2\theta < 22^\circ$, is $a = 24.828(11)$ Å for $\text{Cd}_{32}\text{Cs}_{28}\text{-X}$ and $24.794(2)$ Å for $\text{Cd}_{28}\text{Rb}_{36}\text{-X}$. All unique reflections in the positive octant of an F -centered unit cell for which $2\theta < 50^\circ$, $l > h$, and $k > h$ were recorded. Of the 1382 unique reflections measured for $\text{Cd}_{32}\text{Cs}_{28}\text{-X}$ and 1373 for $\text{Cd}_{28}\text{Rb}_{36}\text{-X}$, only the 637 and 521 reflections respectively, for which $I > 3\sigma(I)$, were used in subsequent structure determination. Absorption corrections (for $\text{Cd}_{32}\text{Cs}_{28}\text{-X}$, $\mu_R = 0.31$, $\rho_{\text{cal}} = 2.034$ g/cm³ and for $\text{Cd}_{28}\text{Rb}_{36}\text{-X}$, $\mu_R = 0.42$, $\rho_{\text{cal}} = 1.924$ g/cm³) were made empirically using a ψ scan.¹⁴ The calculated transmission coefficients ranged from 0.985 to 0.995. This correction had little effect on the

final R indices. Other details are the same as those previously reported.¹⁵

Structure Determination

$\text{Cd}_{32}\text{Cs}_{28}\text{-X}$ (crystal 1). A full-matrix least-squares refinement was initiated by using the atomic parameters of the framework atoms [Si, Al, O(1), O(2), O(3), and O(4)] in dehydrated $\text{Ca}_{18}\text{Ti}_{56}\text{-X}$.¹⁶ Anisotropic refinement converged to an unweighted R_1 index, $((F_o - |F_c|)/F_o)$, of 0.45 and a weighted R_2 index, $(w(|F_o - |F_c||)^2/wF_o^2)^{1/2}$, of 0.54.

A difference Fourier function revealed two large peaks at (0.0, 0.0, 0.0) and (0.220, 0.220, 0.220) with heights of 27.31 eÅ⁻³ and 7.71 eÅ⁻³, respectively. Anisotropic refinement including these Cd^{2+} ions at Cd(1) and Cd(2) converged to $R_1 = 0.24$ and $R_2 = 0.31$ with occupancies of 15.7(1) and 15.5(1), respectively. A subsequent difference Fourier function revealed two additional peaks at (0.263, 0.263, 0.263) with height 23.76 Å⁻³ and (0.163, 0.163, 0.163) with height 16.92 Å⁻³. Inclusion of these peaks as ions at Cs(2) and Cs(1) lowered the error indices to $R_1 = 0.16$ and $R_2 = 0.20$. The occupancy numbers at Cs(2) and Cs(1) were refined to 10.3(1) and 5.60(1), respectively. The remaining Cs^- ion position was found on an ensuing Fourier function at (0.42, 0.125, 0.125) with height 13.4 Å⁻³. Anisotropic refinement of framework atoms and all cations converged to $R_1 = 0.054$ and $R_2 = 0.062$. The occupancies of Cd(1), Cd(2), Cs(1), Cs(2) and Cs(3) were fixed at the values shown in Table 1 considering the cationic charge +92 per unit cell. The final error indices for the 637 reflections for which $I > 3\sigma(I)$ were $R_1 = 0.058$ and $R_2 = 0.065$. The shifts in the final cycle of least-squares refinement were less than 0.1% of their corresponding standard deviations.

$\text{Cd}_{28}\text{Rb}_{36}\text{-X}$ (crystal 2). A full-matrix least-squares refinement was initiated by using the atomic parameters of the framework atoms for the previous crystal of $\text{Cd}_{32}\text{Cs}_{28}\text{-X}$ (crystal 1). Anisotropic refinement converged to an unweighted $R_1 = 0.45$ and a weighted $R_2 = 0.54$. A difference Fourier function revealed one large peak at (0.0, 0.0, 0.0) with height 34.70 Å⁻³.

Anisotropic refinement including this peak as Cd^{2+} ion at Cd(1) converged to $R_1 = 0.28$ and $R_2 = 0.34$ with occupancies of 16.7(2) at Cd(1). A subsequent difference Fourier function revealed three additional peaks at (0.256, 0.256, 0.256) with height 12.21 Å⁻³, (0.232, 0.232, 0.232) with height 12.55 Å⁻³, and (0.216, 0.216, 0.216) with height 9.90 e-3. Inclusion of these peaks as ions at Rb(1), Cd(3) and Cd(2) lowered the error indices to $R_1 = 0.124$ and $R_2 = 0.142$. The occupancy numbers at Rb(1), Cd(3) and Cd(2) were refined to 15.6(4), 4.2(2) and 8.4(2), respectively. On an ensuing difference Fourier function, one peak appeared at Rb(2) (0.421, 0.113, 0.124) with height 8.40 Å⁻³. Anisotropic refinement of the framework atoms and all the cations converged to $R_1 = 0.085$ and $R_2 = 0.111$. The occupancies of Cd(1), Cd(2), Cd(3), Rb(1) and Rb(2) were fixed at the values shown in Table 2 considering the cationic charge per unit cell.

Table 1. Positional, Thermal^a, and Occupancy Parameters(a) Cd₃₂Cs₂₈-X

Atom	Wyc. Pos.	x	y	z	^b U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃	Occupancy varied fixed	
Si	96(g)	-533(1)	1230(1)	340(1)	52(14)	36(14)	22(14)	-15(15)	-10(13)	-35(16)	96	
Al	96(g)	-546(1)	368(1)	1220(1)	175(16)	127(16)	133(15)	-13(15)	-23(16)	-19(18)	96	
O(1)	96(g)	-1111(3)	10(4)	1059(3)	151(44)	411(49)	208(44)	-131(45)	93(35)	-185(45)	96	
O(2)	96(g)	-28(4)	-36(4)	1449(3)	237(41)	234(42)	278(45)	74(43)	6(46)	-23(46)	96	
O(3)	96(g)	-320(3)	658(3)	604(3)	263(45)	92(40)	138(41)	23(40)	77(41)	-7(36)	96	
O(4)	96(g)	-649(3)	832(3)	1714(3)	148(41)	95(40)	176(41)	-25(40)	36(40)	-51(35)	96	
Cd(1)	16(c)	0	0	0	179(5)	179(5)	179(5)	33(6)	33(6)	33(6)	15.7(1)	16
Cd(2)	32(c)	2194(1)	2194(1)	2194(1)	464(10)	464(10)	464(10)	284(13)	284(13)	284(13)	15.5(1)	16
Cs(1)	32(c)	1631(5)	1631(5)	1631(5)	1327(66)	1327(66)	1327(66)	34(81)	34(81)	34(81)	5.60(1)	6
Cs(2)	32(c)	2631(1)	2631(1)	2631(1)	314(12)	314(12)	314(12)	3(13)	3(13)	3(13)	10.3(1)	10
Cs(3)	96(g)	4248(2)	1250	1250	190(28)	697(43)	875(47)	0	0	-51(41)	12.2(2)	12

(b) Cd₂₈Rb₃₆-X

Atom	Wyc. Pos.	x	y	z	^b U ₁₁ or ^d U _{iso}	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃	Occupancy varied fixed	
Si	96(g)	-535(3)	1228(3)	345(3)	148(30)	81(28)	152(31)	3(34)	-38(28)	-41(36)	96	
Al	96(g)	-537(3)	357(2)	1226(3)	81(29)	76(30)	49(29)	-9(28)	-4(34)	-45(36)	96	
O(1)	96(g)	-1093(6)	6(8)	1082(7)	174(100)	689(131)	168(97)	-89(102)	97(70)	-35(100)	96	
O(2)	96(g)	-39(8)	-37(7)	1467(7)	336(99)	280(93)	286(93)	182(87)	24(95)	-18(94)	96	
O(3)	96(g)	-330(6)	632(6)	623(6)	127(82)	119(83)	175(86)	89(78)	-14(81)	-60(74)	96	
O(4)	96(g)	-658(5)	824(5)	1689(5)	-10(68)	-19(68)	13(70)	-26(63)	54(64)	21(58)	96	
Cd(1)	16(c)	0	0	0	130(9)	130(9)	130(9)	26(12)	26(12)	26(12)	16.7(2)	16
Cd(2)	32(c)	2154(5)	2154(5)	2154(5)	45(48)						8.4(2)	8
Cd(3)	32(c)	2320(3)	2320(3)	2320(3)	81(27)						4.2(2)	4
Rb(1)	32(c)	2558(3)	2558(3)	2558(3)	380(25)	380(25)	380(25)	116(33)	116(33)	116(33)	15.6(4)	15
Rb(2)	48(l)	4202(5)	1250	1250	222(56)	1309(115)	1449(125)	0	0	-502(121)	21.3(1)	21

^aPositional and anisotropic thermal parameters are given $\times 10^4$. Numbers in parentheses are the esds in the units of the least significant digit given for the corresponding parameter. ^bThe anisotropic temperature factor = $\exp[-22\pi^2 a^2 (U_{11}h^2 + U_{22}k^2 + U_{33}l^2 + U_{12}hk + U_{13}hl + U_{23}kl)]$. ^cOccupancy factors are given as the number of atoms or ions per unit cell. ^d $U_{iso} = (B_{iso}/8\pi^2)$

The final error indices for the 485 reflections for which $I > 3\sigma(I)$ were $R_1 = 0.086$ and $R_2 = 0.113$. The shifts in the final cycle of least-squares refinement were less than 0.1% of their corresponding standard deviations.

Atomic scattering factors^{18,19} for Si, Al, O⁻, Cd²⁺, Cs⁺ and Rb⁺ were used. All scattering factors were modified to account for anomalous dispersion.²⁰ The final structural parameters are listed in Table 1 and selected interatomic distances and angles are presented in Table 2.

Discussion

Zeolite X is a synthetic version of the mineral faujasite, which has an open, negatively charged framework. The 14-hedron with 24 vertices known as the sodalite cavity or β cage may be viewed as the principal building block of the aluminosilicate framework of zeolites (see Figure 1). These β -cages are connected tetrahedrally at six-rings by bridging oxygens to give double six-rings (D6R's, hexagonal prisms), and, concomitantly, to give 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 vertices 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.

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 a 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 single six-ring (S6R) entrance to the supercage, II in the supercage adjacent to a S6R, III in the supercage opposite a four-ring between two 12-rings, and III' in the vicinity of III but off the twofold axis.^{24,25}

Cd₃₂Cs₂₈-X (crystal 1). In this structure, the mean values of the Si-O and Al-O bond lengths are normal, ca. 1.62 and 1.72 Å, respectively. The individual bond lengths, however, show marked variations: Si-O from 1.59(8) to 1.66(8) Å and Al-O from 1.69(8) to 1.77(8) Å. Thirty-two Cd²⁺ ions coordinate only to O(2) and O(3) in this structure and, as a consequence of these interactions, the Al-O(2), Si-O(2), Al-O(3), and Si-O(3) bonds are somewhat lengthened (see Table 2).

Table 2. Selected Interatomic Distance (Å) and Angles (deg) for $Cd_{32}Cs_{28}\text{-X}$ and $Cd_{28}Rb_{36}\text{-X}$

	$Cd_{32}Cs_{28}\text{-X}$	$Cd_{28}Rb_{36}\text{-X}$
Si-O(1)	1.60(9)	1.64(2)
Si-O(2)	1.64(9)	1.67(2)
Si-O(3)	1.66(8)	1.70(2)
Si-O(4)	1.59(8)	1.63(1)
Average	1.62	1.66
Al-O(1)	1.70(8)	1.67(2)
Al-O(2)	1.72(9)	1.68(2)
Al-O(3)	1.77(8)	1.72(2)
Al-O(4)	1.69(8)	1.66(1)
Average	1.72	1.68
Cd(1)-O(3)	2.358(8)	2.349(15)
Cd(2)-O(2)	2.194(8)	2.171(18)
Cd(3)-O(2)		2.269(17)
Cs(1)-O(2)	3.193(13)	
Cs(2)-O(2)/Rb(1)-O(2)	2.947(8)	2.707(17)
Cs(3)-O(4)/Rb(2)-O(4)	3.143(9)	3.001(16)
O(1)-Si-O(2)	112.3(5)	112.0(1)
O(1)-Si-O(3)	108.5(4)	105.4(8)
O(1)-Si-O(4)	111.1(4)	111.4(8)
O(2)-Si-O(3)	105.2(4)	108.3(8)
O(2)-Si-O(4)	107.6(4)	107.1(8)
O(3)-Si-O(4)	112.1(4)	112.3(8)
O(1)-Al-O(2)	112.9(5)	112.0(1)
O(1)-Al-O(3)	105.7(4)	106.3(8)
O(1)-Al-O(4)	113.2(4)	112.0(7)
O(2)-Al-O(3)	106.3(4)	108.1(8)
O(2)-Al-O(4)	105.5(4)	107.7(8)
O(3)-Al-O(4)	112.3(5)	111.2(8)
Si-O(1)-Al	129.0(5)	128.0(1)
Si-O(2)-Al	138.5(5)	137.0(1)
Si-O(3)-Al	125.8(5)	127.1(9)
Si-O(4)-Al	160.7(5)	158.8(9)
O(3)-Cd(1)-O(3)	90.8(2)	91.3(5)
O(2)-Cd(2)-O(2)	119.7(4)	119.7(7)
O(2)-Cd(3)-O(2)		113.2(7)
O(2)-Cs(1)-O(2)	73.0(2)	
O(2)-Cs(2)-O(2)	80.2(3)	
O(2)-Rb(1)-O(2)		87.8(5)
O(4)-Cs(3)-O(4)	59.1(2)	
O(4)-Rb(2)-O(4)		60.7(4)

Thirty-two Cd^{2+} ions occupy two crystallographic sites and 28 Cs^{-} ions occupy three crystallographic sites. Sixteen Cd^{2+} ions at Cd(1) fill the octahedral site I at the centers of the D6R's (see Figure 2). The octahedral Cd(1)-O(3) distance, 2.358(8) Å, is a little longer than the sum of the ionic radii of Cd^{2+} and O^{2-} , $0.97 + 1.32 = 2.29$ Å,²⁶ indicating a reasonably good fit.

Six Cs^{+} ions at Cs(1) occupy site II'. These positions are located in the sodalite cavity and lie in a threefold position. Each Cs^{-} ion is coordinated to three O(2) framework oxygens at 3.193(13) Å. Ten Cs^{+} ions at Cs(2) occupy site II.

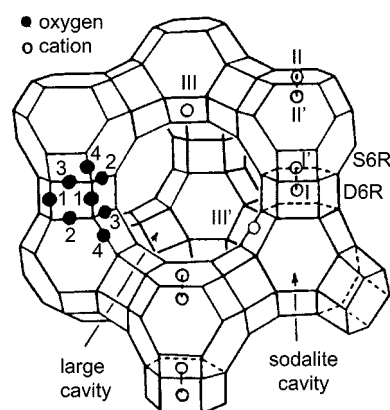


Figure 1. A stylized draws of the framework structure of zeolite X. Near the center of the each line segment is an oxygen atom. Different oxygen atoms are indicated by the numbers 1 to 4. Silicon and aluminum atoms alternate at the tetrahedral intersections, except that a silicon atom substitutes for aluminum atom at about 4% of the Al positions. Extraframework cation positions are labeled with Roman numerals.

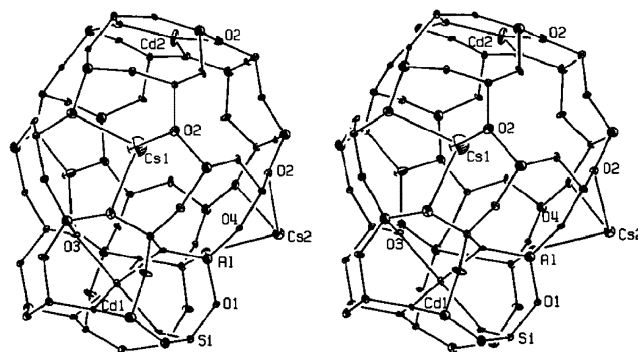


Figure 2. Stereoview of a sodalite cavity with an attached D6R in dehydrated $Cd_{32}Cs_{28}\text{-X}$. One Cd^{2+} ions at Cd(1), two Cd^{2+} ions at Cd(2) (site II) and one Cs^{-} ion at Cs(1) (site II') and one Cs^{-} ion at Cs(2) (site II) are shown. About 75% of double six-ring have this arrangement. Ellipsoids of 20% probability are shown.

The Cs(2)-O(2) distance is 2.947(8) Å. This distance is shorter than the sum of the ionic radii of Cs^{+} and O^{2-} , $1.69 + 1.32 = 3.01$ Å,¹² presumably because Cs(2) is only three coordinate. The remaining 16 Cd^{2+} ions at Cd(2) occupy the 32-fold at site II in the supercage (see Figure 2) and the bond distance of Cd(2)-O(2) is 2.194(8) Å is shorter than the sum (2.29 Å) of the ionic radii of Cd^{2+} and O^{2-} , presumably because Cd(2) is only three-coordinate. Twelve Cs^{-} ions at Cs(3) occupy the 96-fold site III' in the supercage (see Figure 4). An approach distance from Cs(3) to framework oxygen O(4), 3.143(9) Å, is slightly longer than the sum of the ionic radii of Cs^{+} and O^{2-} (see Table 1a and 2).

Recently the structures of $Cd_{46}\text{-X}$,²¹ $Cd_{24.5}Tl_{43}\text{-X}$,²¹ $Ca_{32}K_{28}\text{-X}$ ²² and $Ca_{46}\text{-X}$,²³ were determined. From these it appears that site I is the lowest energy site for most cations, except for the largest. Ca^{2+} ions in $Ca_{46}\text{-X}$ and Cd^{2+} ions in $Cd_{46}\text{-X}$ fill site I, with the remainder going to site II in the supercage, nearly filling it. In $Cd_{24.5}Tl_{43}\text{-X}$, ionic size and charge dominate the competition for sites. The smaller and more highly charged Cd^{2+} ions select their sites "first"

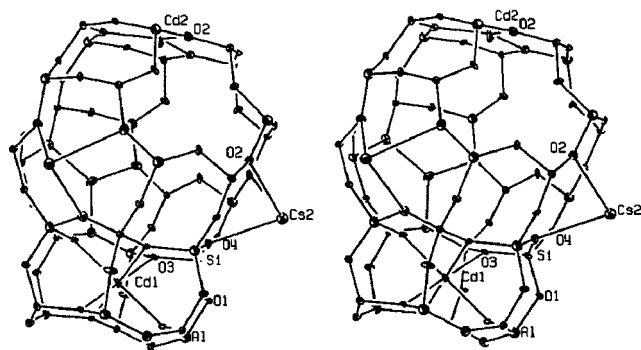


Figure 3. Stereoview of a sodalite cavity with an attached D6R in dehydrated $\text{Cd}_{32}\text{Cs}_{28}\text{-X}$. One Cd^{2+} ions at Cd(1), two Cd^{2+} ions at Cd(2) (site II) and two Cs^+ ions at Cs(2) (site II) are shown. About 25% of sodalite cavities may have this arrangement. Ellipsoids of 20% probability are used.

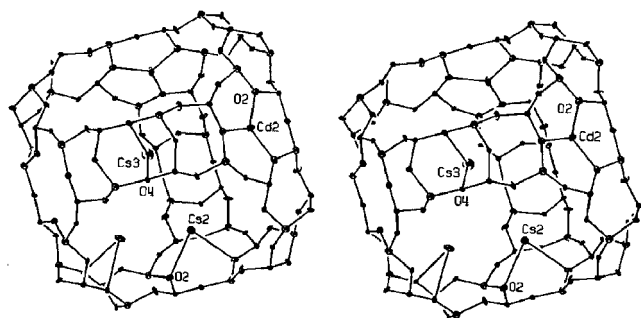


Figure 4. Stereoview of the supercage of dehydrated $\text{Cd}_{32}\text{Cs}_{28}\text{-X}$. Two Cd^{2+} ions at Cd(2) (site II), one Cs^+ ion at Cs(2) (site II) and two Cs^+ ions at Cs(3) (site III') are shown. About 50% of supercages may have this arrangement. Ellipsoids of 20% probability are used.

because they can approach the anionic oxygens of the zeolite framework more closely. They nearly fill the site I position as in $\text{Cd}_{16}\text{-X}$, ascertaining that Cd^{2+} ions prefer site I, the D6R sites I. Once the Cd^{2+} ions have selected their sites, the Ti^{IV} ions finish filling site II, with the remainder going to the least suitable cation site in the structure, site III'. Koller *et al.* studied the location of Na^+ and Cs^+ cations within the dehydrated $\text{Cs}_{40}\text{Na}_{15}\text{-Y}$ by solid state ^{23}Na and ^{133}Cs nuclear magnetic resonance (NMR) spectroscopy and Rietveld method. They found Na^+ cations at site I are replaced by Cs^+ cations at a high cesium exchange level. Upon increasing the calcination temperature of $\text{Cs}_{40}\text{Na}_{15}\text{-Y}$ from 473 to 773 K, the further migration of Cs^+ and Na^+ to site I is observed. Even though the ionic radius of Cs^+ is 1.69 Å, Cs^+ ion can occupy at site I.²⁴

$\text{Cd}_{28}\text{Rb}_{36}\text{-X}$ (crystal 2). In this structure, 28 Cd^{2+} ions occupy three crystallographic sites and 36 Rb^+ ions occupy two different sites. Sixteen Cd^{2+} ions at Cd(1) fill the octahedral site at the centers of the D6R's ($\text{Cd}(1)\text{-O}(3) = 2.349(15)$ Å and $\text{O}(3)\text{-Cd}(1)\text{-O}(3) = 91.3(5)^\circ$). Eight Cd^{2+} ions at Cd(2) occupy the 32-fold site II in the supercage (see Figures 5 and 6): The $\text{Cd}(2)\text{-O}(2)$ distance, 2.171(18) Å, is shorter than the sum of the conventional ionic radii¹² of Cd^{2+} and O^{2-} , 0.97 Å + 1.32 Å = 2.29 Å, presumably because Cd(2) is only three-coordinate. These Cd^{2+} ions are slightly

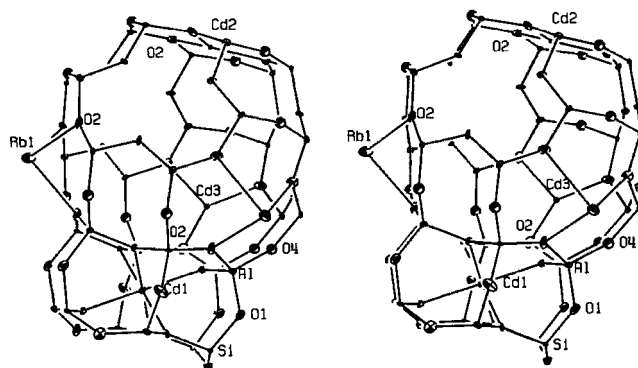


Figure 5. Stereoview of a sodalite cavity with an attached D6R in dehydrated $\text{Cd}_{28}\text{Rb}_{36}\text{-X}$. One Cd^{2+} ions at Cd(1), one Cd^{2+} ion at Cd(2) (site II) and one Cd^{2+} ion at Cd(3) (site II) and two Rb^+ ions at Rb(1) (site II) are shown. About 50% of sodalite cavities may have this arrangement. Ellipsoids of 20% probability are used.

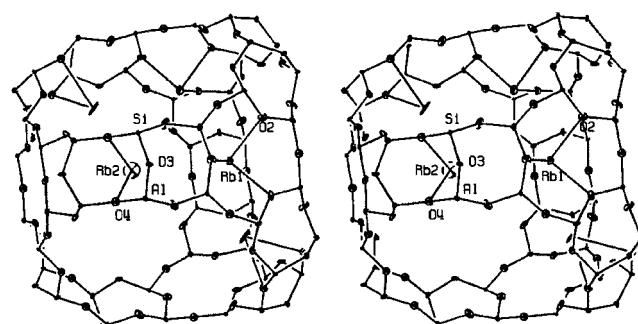


Figure 6. Stereoview of the supercage of dehydrated $\text{Cd}_{28}\text{Rb}_{36}\text{-X}$. Two Rb^+ ions at Rb(1) (site II) and three Rb^+ ions at Rb(2) (site III') are shown. About 50% of supercages may have this arrangement. Ellipsoids of 20% probability are used.

recessed, (0.48) into the supercage from the plane of the three O(2) oxygens (see table 3). The $\text{O}(2)\text{-Cd}(2)\text{-O}(2)$ bond angle, $119.7(7)^\circ$, is nearly trigonal planar. Four Cd^{2+} ions at Cd(3) occupy site II. Four Cd^{2+} ions at Cd(3) occupy the 32-fold site II in the supercage. The $\text{Cd}(3)\text{-O}(2)$ distance is 2.269(17) Å, and $\text{O}(2)\text{-Cd}(3)\text{-O}(2)$ angle is $113.2(7)^\circ$. Compared with the structure of $\text{Cd}_{32}\text{Cs}_{28}\text{-X}$, the sites of Cd^{2+} ions are similar to those of $\text{Cd}_{28}\text{Rb}_{36}\text{-X}$.

Rb(1) is recessed 1.620(4) into the supercage from the S6R plane at O(2) (see Figure 5 and 6). 15 Rb^+ ions lie at

Table 3. Deviations (Å) of Cations from Six-Ring Planes

	$\text{Cd}_{32}\text{Cs}_{28}\text{-X}$	$\text{Cd}_{28}\text{Rb}_{36}\text{-X}$
Cd(1)	at O(3) ^a	1.32(1)
	at O(2) ^b	-0.095(2)
Cd(2)		-0.118(7)
Cd(3)		0.598(4)
Cs(1)	2.322(4)	
Rb(1)		1.620(4)
Cs(2)	1.974(2)	

^aA negative deviation indicates that the atom lies in a D6R. ^bA positive deviation indicates that the atom lies in the supercage and a negative deviation indicates that the atom lies in the sodalite cavity.

Table 4. Distribution of Nonframework Atoms over Sites

Sites	Crystals	
	Cd ₃₂ Cs ₂₈ -X	Cd ₂₈ Rb ₃₆ -X
I	16Cd(1)	16Cd(1)
II	16Cd(2)	8Cd(2)
II	6Cs(1)	4Cd(3)
II	10Cs(2)	15Rb(1)
III	12Cs(3)	21Rb(2)

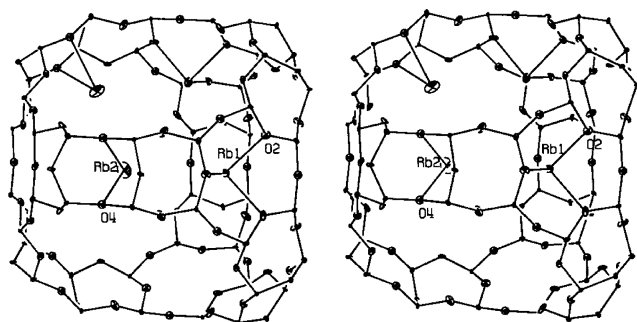


Figure 7. Stereoview of the supercage of dehydrated Cd₂₈Rb₃₆-X. Two Rb⁺ ions at Rb(1) (site II) and two Rb⁺ ions at Rb(2) (site III') are shown. About 37.5% of supercages may have this arrangement. Ellipsoids of 20% probability are used.

Rb(1) (site II). The Rb(1)-O(2) bond distance, 2.707(17) Å, is almost the same as the sum of ionic radii¹² of Rb⁺ and O²⁻, 1.48 Å + 1.32 Å = 2.80 Å. The O(2)-Rb(1)-O(2) bond angle is 87.8(5)°, far less than 120° (trigonal planar), indicating again that the Rb⁺ ion is too large to fit into the plane of this six-ring. 21 Rb⁺ ions at Rb(2) per unit cell lie in the supercage at site III' (see Figure 7). Each of these Rb⁺ ions coordinates to three O(4) oxygens at 3.001(16) Å, longer than the sum of the corresponding ionic radii, 2.80 Å. The angle at Rb(2), O(4)-Rb(2)-O(4), is 60.7(4)°.

This work indicates that all of the Na⁺ ions in zeolite X can readily be replaced by Cd²⁺ and Cs⁺ (or Rb⁺) ions. The size and charge of cations govern the competition for sites in both structures. The smaller and more highly charged Cd²⁺ ions nearly fill site I, with the remainder going to site II, affirming that Cd²⁺ ions prefer site I. The larger Cs⁺ (or Rb⁺) ions, which are less able to balance the anionic charge of zeolite framework because of their size, finish filling the sodalite cavity with some occupancy at site II', and finish filling site II, with the remainder going to the least suitable cation site in the structure sites III and III'. Considering the experimental procedures and the structures of Cd₃₂Cs₂₈-X

and Cd₂₈Rb₃₆-X, Rb⁺ ions have a higher ion-selectivity than Cs⁺ ions in Cd₄₆-X.

Supporting Information Available: Tables of calculated and observed structure factors (5 pages). The supporting materials will be given upon your request to the correspondence author

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