Two Crystal Structures of Dehydrated Zn^{2+}-Exchanged Zeolite X: $Zn_{46}Si_{100}Al_{92}O_{384} \cdot 8$ ZnO and $Zn_{13}Tl_{66}Si_{100}Al_{92}O_{384} \cdot 2$ ZnO

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The crystal structures of fully dehydrated fully Zn^{2+}-exchanged zeolite X, $Zn_{46}Si_{100}Al_{92}O_{384} \cdot 8$ ZnO (Zn_{46}-X$\cdot$8 ZnO; $a = 24.710(4)$ Å), and that of fully dehydrated Zn^{2+}-and Tl^+-exchanged zeolite X, $Zn_{13}Tl_{66}Si_{100}Al_{92}O_{384} \cdot 2$ ZnO ($Zn_{13}Tl_{66}$-X$\cdot$2 ZnO; $a = 24.984(4)$ Å), have been determined by single-crystal X-ray diffraction methods in the cubic space group $Fd\overline{3}$ at 21(1) °C. Zn_{46}-X$\cdot$8 ZnO was prepared by ion exchange in a flowing stream of 0.05 M aqueous $Zn(NO_3)_2$ for 2 days. $Zn_{13}Tl_{66}$-X$\cdot$2 ZnO was similarly prepared using a solution of 0.025 M each in $Zn(NO_3)_2$ and $TlNO_3$. Each crystal was then dehydrated at 400 °C and 2×10^{-6} Torr for 2 days. Their structures were refined to the final error indices $R_1 = 0.052$ and $R_2 = 0.047$, with 292 reflections for Zn_{46}-X$\cdot$8 ZnO, and $R_1 = 0.039$ and $R_2 = 0.034$, with 382 reflections for $Zn_{13}Tl_{66}$-X$\cdot$2 ZnO; $I > 3\sigma(I)$. In the structure of dehydrated Zn_{46}-X$\cdot$8 ZnO, Zn^{2+} ions are located at four different crystallographic sites. Two Zn^{2+} ions lie at the center of a double six-ring (site I, Zn-O = 2.584(10) Å, O-Zn-O = 103.2(4)°). Twenty-eight Zn^{2+} ions are located at site I' displaced from a shared hexagonal face into a sodalite cavity (Zn-O = 1.984(12) Å, O-Zn-O = 108.0(4)°). Eight over-exchanged Zn^{2+} ions, which lie at site II', are recessed *ca.* 0.61 Å into the sodalite cavity from their three O(2) oxygen plane (Zn-O = 2.109(11) Å and O-Zn-O = 109.1(4)°), and each associates with three framework oxygens and also with one nonframework oxygen deeper in the sodalite unit in a distorted tetrahedral arrangement. The remaining sixteen Zn^{2+} ions are found at site II in a supercage (Zn-O = 1.986(10) Å and O-Zn-O = 119.7(5)°). In the structure of a dehydrated $Zn_{13}Tl_{66}$-X$\cdot$2 ZnO, thirteen Zn^{2+} ions are found at site I' adjacent to D6R (Zn-O = 2.036(14) Å and O-Zn-O = 119.8(5)°). Two over-exchanged Zn^{2+} ions, which lie at site II', are recessed *ca.* 0.66 Å into the sodalite cavity from their three O(2) oxygen plane (Zn-O = 2.276(36) Å and O-Zn-O = 109.9(5)°). Tl^+ ions are located at four different crystallographic sites. Nineteen Tl^+ ions lie at site I' in the sodalite cavity (Tl-O = 2.536(13) Å and O-Tl-O = 88.0(4)°). Thirty Tl^+ ions occupy site II, recessed 1.68 Å into a supercage from the three O(2) oxygen plane (Tl-O = 2.678(10) Å and O-Tl-O = 88.0(4)°). Fourteen Tl^+ ions are found at site III deep in the supercage (Tl-O = 2.835(14) Å, O-Tl-O = 75.4(4)°). The remaining three Tl^+ ions are found at site III' in a supercage (Tl-O = 3.007(62) Å, Tl-O = 2.408(59) Å, O-Tl-O = 55.4(13)°).

Introduction

The synthetic zeolite X has a framework structure similar to that of the natural mineral faujasite[1]. Many structural investigations have been devoted to the characterization of cation distributions in faujasite-type zeolites.[2-4]

The knowledge of the three-dimensional structures of zeolites is quite important for the understanding of their properties such as absorption and catalysis, which are sensitive to the nature of the cations, their number, and the distribution in the framework cavities. Cation substitution is one of the methods of modifying physical and chemical properties of zeolites. So, the problem of reactivity and location of multivalent-exchanged ions is of interest from both theoretical and practical points of view. The distribution and coordination of various cations in the framework of faujasite-type zeolites have been widely investigated and reviewed.[2]

Only a few studies of dehydrated Group II cation-exchanged zeolite X are present in the literature.[5-10] Smolin *et al.*[5] determined the crystal structures of Ca-X after dehydration at various temperatures. In a partially dehydrated form, Ca^{2+} ions are located in sites I, I', II, and III. They confirmed that the occupancy at site III decreases with increas-

ing dehydration temperature. In partially dehydrated $Sr_{44.8}$-X[6], Sr^{2+} ions are located in four sites, I, I', II, and II'. Barrer *et al.*[7] reported that Ba^{2+} (r = 1.34 Å) did not exchange completely into zeolite X at room temperature, and that it did not occupy site I in the hydrated zeolite. In a dehydrated crystal of Ba^{2+}-exchanged natural faujasite,[8] and in dehydrated $Ba_{38}Na_{10}$-X[9], Ba^{2+} ions occupy sites I, I', and II. The order of decreasing occupancy of sites for Ba^{2+} ion is $II > I > I'$. Yeom *et al.*[10] determined the crystal structure of fully dehydrated Mg_{46}-X, Ca_{46}-X, and Ba_{46}-X. Their results are summarized in Table 1.

Callograris *et al.* studied the crystal structures of the hydrated and partially dehydrated forms of Cd^{2+}-exchanged zeolites.[11] They compared the occupied sites and occupancies of Cd^{2+} ions and H_2O molecules in the structure of hydrated Cd_{44}-X with those of partially hydrated Cd_{44}-X. They also investigated the migration of Cd^{2+} ions and H_2O molecules during the dehydration. Kwon *et al.*[12] determined the crystal structure of fully dehydrated Cd_{46}-X and $Cd_{24.5}Tl_{43}$-X. Their results are summarized in Table 1.

Peapples-Montgomery and Seff synthesized the fully dehydrated, fully Zn^{2+}-exchanged zeolite Y by the reduction of all H^+ ions in H-Y by zinc vapor.[13] Two different Zn^{2+}

Table 1. Distribution of Cations over Sites

Site	I	I'	II	II'	III	III'
Maximum Occupancy[a]	16	32	32	32	48	96[b]
Tl_{92}-X[c]		31.8(4)	32.1(4)			16.3(5)
						10.6(6)
Mg_{46}-X[d]	14.7(7)	4.2(11)	28.2(11)			
Ca_{46}-X[e]	16.3(5)		31.3(7)			
Ba_{46}-X[f]	13.6(1)	1.6(2)	28.9(2)			
Cd_{46}-X[g]	16.6(2)		29.5(2)			
Zn_{46}-X·8ZnO[h]	2.5(2)	27.8(3)	16.9(3)	8.7(2) Zn^0		
$Zn_{13}Tl_{66}$-X·2 ZnO[i]		13.5(1) Zn^+, 18.5(1) Tl^+	29.2(1) Tl^+	2.2(3) Zn^0		14.0(2)
						2.7(3) Tl^+
$Cd_{24.5}Tl_{43}$-X[j]	14.6(7) Cd^{2+}		10.8(9) Cd^{2+}, 21.1(4) Tl^+		18.1(4) Tl^+	

[a]Ions per unit cell. [b]Due to crowding, all 96 sites may not be available. [c]Ref. 18. [d]Ref. 10. [e]Ref. 10. [f]Ref. 10. [g]Ref. 12. [h]Ref. This work. [i]Ref. This work. [j]Ref. 12.

positions were found in the structure. The Zn(1) position is located on a threefold axis in the sodalite unit adjacent to a single 6-ring (site II'). The Zn(2) position is also on a three-fold axis in the sodalite unit, but is adjacent to a double 6-ring (site I').

This work investigated the cation position in the crystal structure of the dehydrated fully Zn^{2+}-exchanged zeolite X, and Zn^{2+} and Tl^+-exchanged zeolite X. The selective positions of Zn^{2+} and Tl^+ ions within zeolite X were determined. Because the ionic radii of Zn^{2+} and Tl^+ ions are quite different, precise and reliable crystallographic determination should be easy to perform.

Experimental Section

Large single crystals of synthetic sodium zeolite X, stoichiometry of $Na_{92}Al_{92}Si_{100}O_{384}$, were prepared in St. Petersburg, Russia.[14] Each of two single crystals, colorless octahedra about 0.20 mm in cross-section, was lodged in a fine Pyrex capillary. An exchange solution of 0.05 M $Zn(NO_3)_2$ was filtered through a membrane filter for crystal 1 (Zn_{46}-X·8ZnO). Crystal 2 of composition $Zn_{13}Tl_{66}$-X·2 ZnO was prepared using an exchange solution whose $Zn(NO_3)_2$: $TlNO_3$ mole ratio was 1 : 1 with a total concentration of 0.05 M. Ion exchange was accomplished by flow methods; the solution was allowed to flow past each crystal at a velocity of approximately 10 mm/sec for 2 days at 24(1) °C. Each crystal was dehydrated at 400 °C for crystal 1 and crystal 2 under the constant pressure of 2×10^{-6} Torr for 36 h. After cooling to room temperature, each crystal, still under vacuum, was sealed in its capillary by a torch. The two crystals were colorless.

The space group $Fd\overline{3}$ 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, alternation of Si and Al and (b) the observation that these crystals, like all other crystals from the same batch, do not have intensity symmetry across (110) and therefore lack 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 a graphite monochromator, using Mo Kα radiation (Kα_1, $\lambda = 0.70930$ Å, Kα_2, $\lambda = 0.71359$ Å). The cubic unit cell constants determined by a least-squares refinement of 25 intense reflections for which $14° < 2\theta < 24°$ are 24.710(4) Å for Zn_{46}-X·8 ZnO and 24.984(4) Å for $Zn_{13}Tl_{66}$-X·2 ZnO.

The ω-2θ scan technique was used. The data were collected using variable scan speeds. Most reflections were observed at slow scan speeds, ranging between 0.24 and 0.34 deg min^{-1} in ω. The intensities of three reflections in diverse regions of reciprocal space were recorded every 3h to monitor crystal and instrument stability. Only small random fluctuations of these check reflections were noted during the course of data collection. All unique reflections in the positive octant of an F-centered unit cell of which $2\theta <$ 50°, l > h, and k > h were examined.

The raw data were corrected for Lorentz and polarization effects, including incident beam monochromatization, and the resultant estimated standard deviations were assigned to each reflection by the computer programs GENESIS and BEGIN.[15] Of the 1344 unique reflections examined for Zn_{46}-X·8 ZnO and 1386 for $Zn_{13}Tl_{66}$-X·2 ZnO, only the 292 and 382 reflections, respectively, for which I > 3σ(I) were used in subsequent structure determinations.

Structure Determination

Zn_{46}-X·8 ZnO (Crystal 1). Full matrix least-squares refinement was initiated using the atomic parameters of the framework atoms [Si, Al, O(1), O(2), O(3), and O(4)] in dehydrated $Rb_{71}Na_{21}Si_{100}Al_{92}O_{384}$-X.[16] Isotropic refinement of the framework atoms converged to an unweighted R_1 index, $\Sigma(|F_o-|F_c||)/\Sigma F_o$, of 0.351 and a weighted R_2 index, $(\Sigma w(F_o-|F_c|)^2/\Sigma wF_o^2)^{1/2}$, of 0.422.

The initial different Fourier function revealed two large peaks at Zn(2) (0.058, 0.058, 0.058) and Zn(3) (0.199, 0.199, 0.199), with peak heights of 9.8 eÅ^{-3} and 8.6 eÅ^{-3}, respectively. Isotropic refinement of the framework atoms, Zn(2), and Zn(3) (see Table 2 (a)) converged to $R_1 = 0.17$ and $R_2 = 0.18$.

Table 2. Positional,Thermal, and Occupancy Parameters[a]
(a) Crystal 1

Atom	Wyc. Pos.	x	y	z	[b]U_{11} or U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	[c]Occupancy	
											varied	fixed
Si	96(g)	-496(2)	1245(2)	364(2)	194(28)	162(26)	218(27)	-8(36)	-2(27)	30(39)		96
Al	96(g)	-522(2)	382(2)	1226(3)	188(29)	122(27)	154(27)	32(28)	-28(38)	-15(37)		96
O(1)	96(g)	-956(4)	-11(5)	1019(4)	505(81)	320(72)	427(81)	26(64)	-192(61)	-17(64)		96
O(2)	96(g)	7(4)	11(4)	1507(3)	306(60)	242(59)	86(53)	130(59)	65(56)	51(54)		96
O(3)	96(g)	-191(5)	704(4)	749(4)	738(85)	148(68)	217(67)	116(63)	231(67)	39(62)		96
O(4)	96(g)	-707(4)	777(4)	1687(4)	314(67)	311(69)	285(67)	-69(67)	47(67)	-147(55)		96
Zn(1)	16(c)	0	0	0	399(123)	399(123)	399(123)	41(147)	41(147)	41(147)	2.5(2)	2.0
Zn(2)	32(e)	586(2)	586(2)	586(2)	991(18)	991(18)	991(18)	479(25)	479(25)	479(25)	27.8(3)	28.0
Zn(3)	32(e)	1996(3)	1996(3)	1996(3)	91(28)	91(28)	91(28)	51(35)	51(35)	51(35)	8.7(2)	8.0
Zn(4)	32(e)	2186(3)	2186(3)	2186(3)	886(24)	886(24)	886(24)	763(29)	763(29)	763(29)	16.9(3)	16.0
O(5)	32(e)	1488(19)	1488(19)	1488(19)	697(444)						11.0(9)	8.0

(b) Crystal 2

Atom	Wyc. Pos.	x	y	z	[b]U_{11} or U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	Occupancy	
											varied	fixed
Si	96(g)	-524(2)	1247(2)	357(2)	134(27)	127(24)	59(23)	-30(24)	-3(23)	-40(23)		96
Al	96(g)	-533(2)	369(2)	1239(2)	86(26)	32(23)	62(24)	-13(24)	-10(24)	4(23)		96
O(1)	96(g)	-1042(4)	-4(6)	1023(5)	171(62)	521(81)	266(67)	-49(85)	-101(57)	-65(89)		96
O(2)	96(g)	-14(5)	-13(6)	1459(4)	124(47)	243(52)	225(53)	120(72)	73(75)	1(82)		96
O(3)	96(g)	-266(5)	730(5)	706(5)	288(70)	144(61)	120(60)	59(63)	32(63)	1(62)		96
O(4)	96(g)	-715(5)	773(5)	1744(5)	280(69)	162(66)	238(67)	-26(71)	-40(71)	-27(59)		96
Zn(1)	32(e)	409(3)	409(3)	409(3)	435(30)	435(30)	435(30)	228(38)	228(38)	228(38)	13.5(1)	13.0
Zn(2)	32(e)	1990(15)	1990(15)	1990(15)	72(109)	72(109)	72(109)	295(134)	295(134)	295(134)	2.2(3)	2.0
Tl(1)	32(e)	736(1)	736(1)	736(1)	300(6)	300(6)	300(6)	-19(7)	-19(7)	-19(7)	18.5(1)	19.0
Tl(2)	32(e)	2532(1)	2532(1)	2532(1)	317(2)	317(2)	317(2)	-36(6)	-36(6)	-36(6)	29.2(1)	30.0
Tl(3)	48(f)	4100(2)	1115(4)	1377(5)	241(34)	944(80)	1536(90)	-170(43)	224(54)	-258(54)	14.0(2)	14.0
Tl(4)	96(g)	4165(23)	824(24)	873(23)	1254(170)						2.7(3)	3.0

[a]Positional 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. [b]The anisotropic temperature factor = $\exp[(-2\pi^2/a^2)(U_{11}h^2 + U_{22}k^2 + U_{33}l^2 + U_{12}hk + U_{13}hl + U_{23}kl)]$. [c]Occupancy factors are given as the number of atoms or ions per unit cell.

A subsequent difference Fourier synthesis showed a peak at Zn(4) (0.22, 0.22, 0.22), with a peak height of 5.1 eÅ^{-3} and a peak at Zn(1) (0.0, 0.0, 0.0), with a peak height of 3.1 eÅ^{-3}. Simultaneous refinement of positional and anisotropic thermal parameters for the framework atoms, Zn(1), Zn(2), Zn(3), and Zn(4) converged to the error indices $R_1 = 0.057$ and $R_2 = 0.060$.

A subsequent difference Fourier synthesis showed a peak at O(5) (0.15, 0.15, 0.15), with a peak height of 1.3 eÅ^{-3}. Simultaneous refinement of positional and anisotropic thermal parameters for the framework atoms, Zn(1), Zn(2), Zn(3), and Zn(4), and isotropic refinement of O(5) converged to the error indices $R_1 = 0.051$ and $R_2 = 0.048$ (see Table 2(a)). The final refinement as shown in Table 2 was done using 694 reflections for which $I > 0$ to make the most use of the diffraction data: $R_1 = 0.159$ and $R_2 = 0.055$. This allowed the esds to decrease to about 35% of their former values.

An absorption correction ($\mu = 2.25$ mm^{-1} and $\rho_{cal} = 1.59$ g/cm^3) was made empirically using a Ψ scan. The calculated transmission coefficients ranged from 0.90 to 0.99. This correction had little effect on the final R values.

Zn₁₃Tl₆₆-X·2 ZnO (Crystal 2). Full matrix least-squares refinement was initiated using the atomic parameters of the framework atoms [Si, Al, O(1), O(2), O(3), and O(4)] in the dehydrated Zn$_{46}$-X·8ZnO. Isotropic refinement of the framework atoms converged to $R_1 = 0.620$ and $R_2 = 0.708$. A different Fourier function showed the position of Tl$^+$ ions at Tl(2) (0.25, 0.25, 0.25), with a peak height of 21.8 eÅ^{-3}, Tl$^+$ ions at Tl(1) (0.07, 0.07, 0.07), with a peak height of 16.2 eÅ^{-3}. Anisotropic refinement of the framework atoms, and isotropic refinement of Tl(1) and Tl(2) converged to $R_1 = 0.12$ and $R_2 = 0.15$. A subsequent difference Fourier function showed the position of Zn^{2+} ions at Zn(2) (0,04, 0.04, 0.04), with a peak height of 6.8 eÅ^{-3}, and Tl$^+$ ions at Tl(3) (0.41, 0.11, 0.13), with a peak height of 5.8 eÅ^{-3}. These were stable in least-squares refinement, and anisotropic refinement of framework atoms and isotropic refinement of Zn(2), Tl(1), Tl(2), Tl(3), and Tl(4) converged to $R_1 = 0.052$ and $R_2 = 0.045$ (see Table 2(b)).

It is not very difficult to distinguish Zn^{2+} from Tl^+ ions, for several reasons. First, their ionic radii, $Zn^{2+} = 0.74$ Å and $Tl^+ = 1.47$ Å,[17] are different. Second, the approach distances between these ions and zeolite oxide ions in the previous Zn_{46}-X·8 ZnO (see Tables 2(a) and 3) and Tl_{92}-X[18] have been determined and are indicative. Finally, the requirement that 92 monovalent metal ions (or 46 divalent metal ions)

Table 3. Selected Interatomic Distance (Å) and Angles (ºC)

	Crystal 1	Crystal 2
Si-O(1)	1.569(12)	1.616(16)
Si-O(2)	1.652(12)	1.659(16)
Si-O(3)	1.667(12)	1.674(14)
Si-O(4)	1.582(12)	1.623(14)
Al-O(1)	1.669(12)	1.650(16)
Al-O(2)	1.755(12)	1.712(16)
Al-O(3)	1.776(12)	1.733(14)
Al-O(4)	1.690(12)	1.686(15)
Zn(1)-O(3)	2.584(10)	
Zn(2)-O(3)	1.984(12)	2.036(14)
Zn(3)-O(2)	2.109(11)	2.276(36)
Zn(4)-O(2)	1.986(10)	
Zn(3)-O(5)	2.173(27)	
Tl(1)-O(3)		2.536(13)
Tl(2)-O(2)		2.678(10)
Tl(3)-O(4)		2.835(14)
Tl(4)-O(1)		3.007(62)
Tl(4)-O(4)		2.408(59)
O(1)-Si-O(2)	112.0(6)	112.9(7)
O(1)-Si-O(3)	111.3(6)	109.7(7)
O(1)-Si-O(4)	112.9(6)	110.0(7)
O(2)-Si-O(3)	102.3(6)	103.8(6)
O(2)-Si-O(4)	108.4(6)	109.2(6)
O(3)-Si-O(4)	109.3(6)	111.1(7)
O(1)-Al-O(2)	115.0(6)	111.9(7)
O(1)-Al-O(3)	109.3(6)	109.5(6)
O(1)-Al-O(4)	116.0(6)	111.8(7)
O(2)-Al-O(3)	102.2(5)	104.3(6)
O(2)-Al-O(4)	104.3(5)	107.5(6)
O(3)-Al-O(4)	109.3(5)	111.5(6)
Si-O(1)-Al	151.0(8)	143.1(8)
Si-O(2)-Al	129.6(6)	138.7(7)
Si-O(3)-Al	122.2(7)	130.3(8)
Si-O(4)-Al	144.7(7)	145.2(8)
O(3)-Zn(1)-O(3)	103.2(4)	
O(2)-Zn(2)-O(2)	108.0(4)	119.8(5)
O(3)-Zn(2)-O(3)	109.1(4)	109.9(5)
O(2)-Zn(3)-O(2)	119.7(5)	
O(3)-Tl(1)-O(3)		88.0(4)
O(2)-Tl(2)-O(2)		88.0(4)
O(4)-Tl(3)-O(4)		74.5(4)
O(1)-Tl(4)-O(4)		55.4(13)

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

per unit cell be found does not allow the major positions to be refined to acceptable occupancies with an alternative assignment of ionic identities.

From successive difference Fouriers, one peak was found at (0.03, 0.03, 0.03), height = 1.61 eÅ^{-3}, which was refined as Zn(3). Simultaneous refinement of positional and an isotropic thermal parameter for the framework atoms, Zn(2), Zn(3), Tl(1), Tl(2) and Tl(3), and isotropic refinement of Tl(4), converged to the error indices $R_1 = 0.039$ and $R_2 = 0.034$. The occupancy numbers were reset and fixed at the values shown in Table 2(b). 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 $R_1 = 0.039$ and $R_2 = 0.034$. The final difference function was featureless except for a peak at (0.33, 0.33, 0.33) of height 0.72 eÅ^{-3} This peak was not refined in the least-squares refinement.

The final refinement as shown in Table 2(b) was done using 782 reflections, for which $I > 0$, to make the most use of the diffraction data: $R_1 = 0.137$ and $R_2 = 0.040$. This allowed the esds to decrease to about 35% of their former values.
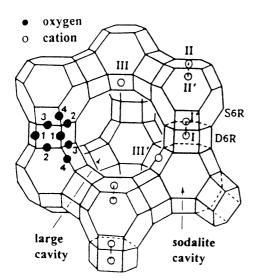
Atomic scattering factors for Si, Al, O^-, Tl^+, and Zn^{2+} were used. Atomic scattering factors were modified to account for anomalous dispersion. The final structural parameters and selected interatomic distances and angles are presented in Tables 2 and 3.

An absorption correction ($\mu = 14.49$ mm^{-1} and $\rho_{cal} = 2.49$ g/cm^3) was made empirically using a Ψ scan. The calculated transmission coefficients ranged from 0.92 to 0.98. This correction had little effect on the final R values.

Discussion

Zeolite X is a synthetic counterpart of the naturally occurring mineral faujasite. The 14-hedra with 24 vertices known as the sodalite cavities or 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 halfway 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 supercages, 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 as shown in Figure 1: site I at the center of a D6R, site I′ in the sodalite cavity on the opposite side of one of the D6Rs 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 on a twofold axis
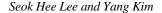
Figure 1. Framework structure of zeolite X. Near the center of the each line segment is an oxygen atom. The different oxygen atoms are indicated by the numbers 1 to 4. Silicon and aluminum atoms alternate the tetrahedral intersections, except that Si substitutes for about 4% of the Al's. Extraframework cation positions are labeled with Roman numerals. Site IV, difficult to indicate, is at the center of the supercage.
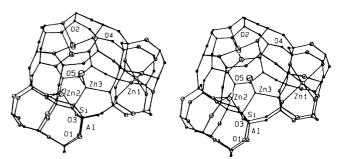

Figure 2. A stereoview of a sodalite cavity with two attached D6R in dehydrated Zn_{46}-X·8 ZnO. Shown are one Zn^{2+} ion at Zn(1) (site I), three Zn^{2+} ions at Zn(2) (site I′), one Zn^{2+} ion at Zn(3) (site II′), and one oxygen at O(5) (connected with Zn(3)). About 50% of the sodalite cavities may have this arrangement. Ellipsoids of 20% probability are shown.

Figure 3. A stereoview of the supercage of the dehydrated Zn_{46}-X·8 ZnO. One Zn^{2+} ion at Zn(3) (site II′), two Zn^{2+} ions at Zn(4) (site II), and one nonframework oxygen O(5) are shown. All of the supercages have this arrangement. Ellipsoids of 20% probability are shown.

opposite a four-ring between two 12-rings, III′ somewhat or substantially distant from III but otherwise near the wall of supercage or the edge of a 12-ring.[19,20]

In the dehydrated structure of Zn_{46}-X·8 ZnO, Zn^{2+} ions are found at four different crystallographic sites. Two Zn^{2+} ions at Zn(1) are at the center of the double six-oxygen ring (D6R). Zn^{2+} ions at Zn(2) are at site I′, which is displaced from a shared hexagonal face into the sodalite cage. Every site I is surrounded by two sites of I′. The neighboring positions I and I′ cannot be occupied by cations simultaneously, because the resulting intercationic distance would be too short (2.56 Å). On the basis of these considerations, the cation distributions in sites I and I′ become comparable in all the analyses. Sites I and I′ are 16-fold and 32-fold positions, respectively. This mutual blocking will, however, limit the site occupation of the linked group I + I′ to not more than 32 by the inequality $n(I′) \leq 2 [16-n(I)]$, where $n(I′)$ and $n(I)$ are the number of cations in the sites per unit cell. From the inequality relationship mentioned above, the observed cation population of site I′ is equal to 28.0 (see Table 2), and the cation occupancy of site I must be less than 2.0. The octahedral Zn(1)-O(3) distance, 2.584(10) Å, is longer than the sum of the ionic radii of Zn^{2+} and O^{2-},[17] 0.74 Å + 1.32 = 2.06 Å.
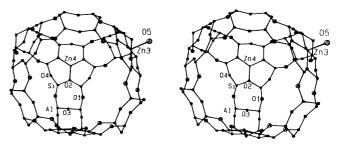
Twenty-eight Zn^{2+} ions at Zn(2) are found at site I′; each is recessed *ca.* 0.71 Å into the sodalite unit from its three-O(3) plane. Each Zn^{2+} ion coordinates at 1.984(12) Å to those three oxygens..

Eight over-exchanged Zn^{2+} ions, which lie at site II′, are recessed *ca.* 0.61 Å into the sodalite cavity from their three O(2) oxygen plane (Zn-O = 2.109(11) Å and O-Zn-O = 109.1(4)°), each associated with three oxygens of the zeolite framework and one nonframework oxygen (O(5)) deeper in

the sodalite unit in a distorted tetrahedral arrangement (see Figures 2 and 3). The bond distances of Zn(3)-O(5) = 2.173(27) Å is a little longer than the Zn-O distance in zinc oxide, 1.98 Å.

During ion exchange, 16 OH^- ions per unit cell accompanied the Zn^{2+} ions into the zeolite, either as $ZnOH^+$ or $Zn(OH)_2$. Accordingly, eight Zn^{2+} ions more than needed for conventional complete ion exchange were needed to balance the additional anionic charge. When H_2O was driven off by vacuum dehydration at elevated temperatures, eight oxide ions remained per unit cell. Thus, zinc oxide molecules might be formed during dehydration process as follows:

$$Zn(OH)_2 \rightarrow ZnO + H_2O$$
$$2 Zn(OH)^+ \rightarrow ZnO + Zn^{2+} + H_2O$$

Sixteen Zn^{2+} ions at Zn(4) per unit cell occupy the threefold axes in the supercage (see Figure 3). The Zn(4)-O(2) distance is 1.986(10) Å.

Peapples-Montgomery and Seff studied the structure of the fully dehydrated Zn^{2+}-exchanged zeolite Y.[13] The Zn(1) position is on a threefold axis in the sodalite unit, 0.87 Å from the plane of the single 6-ring, at site II′. The Zn(2) position is also on a threefold axis inside in the sodalite unit, but opposite a double 6-ring at site I′ and 1.15 Å from the nearer 6-ring plane. The position of Zn(1) of the dehydrated Zn-Y corresponds to the position of Zn(3) of the dehydrated Zn_{46}-X·8 ZnO. The position of Zn(2) of the dehydrated Zn-Y is

corresponding to the position of Zn(2) of the dehydrated Zn_{46}-X·8 ZnO.

Recently Seff, Bae and Chen have also studied a crystal structure of the dehydrated Zn^{2+} exchanged zeoliote X.[21] Unlike this study, they have exchanged Zn^{2+} ions at 80 °C using $Zn(NO_3)_2$ aqueous solution. Number of Zn^{2+} ions per unit cell upon ion exchange is 54, which is exactly same as in the present crystal. However, because of higher temperature ion-exchange, the crystal was much hurt after dehydration, the framework was dealuminated, and the long-range Si/Al ordering was lost, resulting in a change of the space group. Its cell constants also became smaller (a = 24.718 Å). The structure was solved using with $Fd\overline{3}m$ space group. Seff *et al*. reported that Zn_{54}-X upon dehydration became Zn_{56}-X and the whole framework composition changed after aluminates came out as follows:
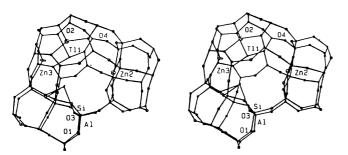
24 $Zn_{46}Si_{100}Al_{92}O_{384}$·8Zn(OH)$_2$(H$_2$O)$_4$ →

23 $Zn_{56}Si_{104}Al_{88}O_{384}$·8HAlO$_4$·8H + 4 Zn_2SiO_4 + 4 H_2SiO_3
+772 H_2O

In their structure, about 56 Zn^{2+} ions occupy three crystallographic sites: 30 almost fill site I′, 23 nearly three quarter fill site II′, and the remaining three occupy site II. In this structure, each sodalite unit contains a monomeric tetrahedral aluminate anion (AlO_4^-) at its center. Unlike the present crystal, Seff's crystal was much more hydrolyzed during the dehydration process.
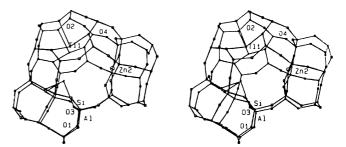
In the dehydrated structure of $Zn_{13}Tl_{66}$-X·2 ZnO, Zn^{2+} ions are found at one crystallographic site and Tl^+ ions are located at four different crystallographic sites. Thirteen Zn^{2+} ions occupy site I′. These cations are trigonally coordinated to their respectively set of three O(3) framework oxygens at 2.036(13) Å.

The Zn(2) occupy site II' in the sodalite cavity with occupancy of 2.0. This position corresponds to the position of Zn(3) of the dehydrated Zn_{46}-X·8 ZnO. Perhaps it is conjectured that two Zn^{2+} ions that lie at site II′ are coordinated by oxygen. But we could not locate nonframework oxygen in the sodalite cavity crystallographically (see Figure 5).
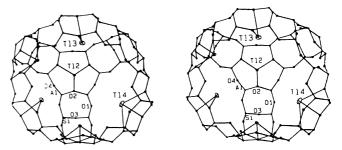
Tl^+ ions at Tl(1) occupy site I′. These positions are located in the sodalite cavity and lie on threefold axes. Each Tl^+ ion is coordinated to three O(3) framework oxygens at 2.536(13)

Figure 5. A stereoview of a sodalite cavity with two attached D6R in dehydrated $Zn_{13}Tl_{66}$-X·2 ZnO are shown. One Zn^{2+} ion at Zn(2) (site I′) and three Tl^+ ions at Tl(1) (site I′) are shown. About 37.5% of the sodalite cavities may have this arrangement. Ellipsoids of 20% probability are shown.

Figure 6. A stereoview of the supercage of the dehydrated $Zn_{13}Tl_{66}$-X·2 ZnO. Three Tl^+ ions at Tl(2) (site II), two Tl^+ ions at Tl(3) (site III′) and one Tl^+ ions at Tl(4) (site III′) are shown. About 25% of the supercages have this arrangement. Ellipsoids of 20% probability are shown.
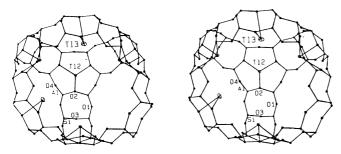
Å. This distance is shorter than the sum of the ionic radii, 1.47 + 1.32 = 2.79 Å. This indicates that each Tl^+ ion coordinates strongly to its three O(3) oxygens, as would be expected by the low coordinates number. The occupancy number of Tl(1) is 19.0. Both Zn(1) and Tl(1) positions are on threefold axes. They are very close together. Therefore, they can not occupied site I′ simultaneously. The sum of the occupancies of Zn(1) and Tl(1) should not exceed 32.

Tl^+ ions at Tl(2) lie at site II, each of which is 1.51 Å recessed into a supercage from a three O(2) oxygen plane (see Figure 6). Each Tl^+ ions coordinates only three O(2)'s at 2.678(10) Å and the bond angle of O(2)-Tl(2)-O(2) is 86.5°. The distance of 2.678(10) Å is slightly shorter than the sum of the ionic radii of Tl^+ and O^{2-}, 2.79 Å and this would be also expected by the low coordinates number. The occupancy is 30.0 per unit cell. These positions (II + II′) are almost fully occupied.

Fourteen Tl^+ ions at Tl(3) lie at site III′ in the supercage (see Figure 7). An approach distance from Tl(3) to the framework oxygen O(4) is slightly longer than the sum of the ionic radii of Tl^+ and O^{2-} (Tl(3)-O(4) = 2.835(14) Å). This position is a 48-fold position.

Three Tl^+ ions at Tl(4) lie at site III′ in the supercage (see Figure 6). The Tl^+ ions at Tl(4) bind strongly to O(4). The Tl(4)-O(1) and Tl(4)-O(4) distances are 3.007(62) Å and 2.408(59) Å, respectively.

In the structures of Cd_{46}-X and $Cd_{24.5}Tl_{43}$-X,[12] the smaller

Figure 4. A stereoview of a sodalite cavity with two attached D6R in dehydrated $Zn_{13}Tl_{66}$-X·2 ZnO. Two Zn^{2+} ions at Zn(2) (site I′), one Zn^{2+} ion at Zn(3) (site II′) and two Tl^+ ions at Tl(1) (site I′) are shown. About 25% of the sodalite cavities may have this arrangement. Ellipsoids of 20% probability are shown.

Figure 7. A stereoview of the supercage of the dehydrated $Zn_{13}Tl_{66}$-X·2 ZnO. Four Tl^+ ions at Tl(2) (site II) and two Tl^+ ions at Tl(3) (site III′) are shown. About 37.5% of the supercages have this arrangement. Ellipsoids of 20% probability are shown.

and more hightly charged Cd^{2+} ions (r = 0.97 Å) nearly fill site I, with the remainder going to the site II as in Cd_{46}-X, affirming that Cd^{2+} ions prefer site I. The larger Tl^+ ions, which are less able to balance the anionic charge of the zeolite framework because of their size, finish satisfying the D6Rs with some occupancy at I′, and finish filling site II, with the remainder going to the least suitable cation site in the structure, site III. In the present structures, Zn^{2+} ions prefer to occupy sites I′ and Tl^+ ions prefer to occupy sites II. Unlike Cd^{2+} ions, Zn^{2+} ion (r = 0.74 Å) may be too small for site I which is at the center of the rigid double six-rings. The smaller Zn^{2+} ions lie closer to framework oxygens than larger Tl^+ ions. Similar to $Cd_{24.5}Tl_{43}$-X,[12] the remaining Tl^+ ions in the structure of $Zn_{15}Tl_{66}$-X go to the least suitable cation site site III′ in the supercage.

This study shows the selective sites of Zn^{2+} and Tl^+ ions in zeolite X. In the dehydrated Zn_{46}-X·8 ZnO structure, Zn^{2+} ions are located at sites I, I′, II′, and II with the occupancy of 2, 28, 8 and 16, respectively (see Table 2(a)). In the dehydrated structure of $Zn_{13}Tl_{66}$-X·2 ZnO, Zn^{2+} ions are found at sites I′ and II′. On the other hand, Tl^+ ions occupy four different sites; I′, II, and two different III′s.

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