제올라이트 X의 두 개의 무수물 $Ca_{18}Tl_{56}Si_{100}Al_{92}O_{384}$ 와 $Ca_{32}Tl_{28}Si_{100}Al_{92}O_{384}$의 결정구조

崔銀暎 · 金 洋*

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Two Anhydrous Zeolite X Crystal Structures, $Ca_{18}Tl_{56}Si_{100}Al_{92}O_{384}$ and $Ca_{32}Tl_{28}Si_{100}Al_{92}O_{384}$

Eun young Choi and Yang Kim*

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

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요 약. Ca^{2+} 이온과 Tl^+ 이온으로 치환되고 완전히 진공 탈수된 제올라이트 X 결정 $Ca_{18}Tl_{56}Si_{100}Al_{92}O_{384}$ ($Ca_{18}Tl_{56}$-X; a=24.883(4) Å)와 $Ca_{32}Tl_{28}Si_{100}Al_{92}O_{384}$ ($Ca_{32}Tl_{28}$-X; a=24.973(4) Å)의 구조를 21(1) °C에서 입방공간군 $Fd\bar{3}$을 사용하여 단결정 X-선 회절법으로 해석하고 그 구조를 정밀화 하였다. $Ca_{18}Tl_{56}$-X 결정은 0.045 M $Ca(NO_3)_2$와 0.005 M $TlNO_3$ 혼합용액으로 흐름법을 이용하여 이온 교환하였다. $Ca_{32}Tl_{28}$-X는 이와 유사하게 0.0495 M $Ca(NO_3)_2$와 0.0005 M $TlNO_3$ 혼합용액을 사용하였다. 각 결정은 360 °C, 2×10^{-6} Torr에서 탈수시켰다. $Ca_{18}Tl_{56}$-X 및 $Ca_{32}Tl_{28}$-X 결정 구조는 각각 $I > 3\sigma$ (I)인 382 및 472개의 회절 반사점을 사용하여 각각 R_1=0.039, R_2=0.036 및 R_1=0.046, R_2=0.045의 최종 오차 지수 값을 얻었다. 탈수된 $Ca_{18}Tl_{56}$-X 및 $Ca_{32}Tl_{28}$-X 결정 구조에서, Ca^{2+} 이온과 Tl^+ 이온은 서로 틀리는 6개의 결정학적 자리에 위치한다. 16개의 Ca^{2+} 이온은 D6R의 중심인 팔면체 자리 I을 채운다 ($Ca_{18}Tl_{56}$-X : Ca-O=2.42(1) Å 및 O-Ca-O=93.06(4)°; $Ca_{32}Tl_{28}$-X : Ca-O=2.40(1) Å 및 O-Ca-O=93.08(3)°). $Ca_{18}Tl_{56}$-X 구조에서는 2개의 Ca^{2+} 이온은 자리 II (Ca-O=2.35(2) Å 및 O-Ca-O=111.69(2)°)를 점유하고 26개의 Tl^+ 이온은 큰 동공 내 마주보는 S6R의 자리 II에 점유한다. 각기 3개의 산소로 만들어지는 평면으로부터 1.493 Å 떨어져 있다(Tl-O=2.70(8) Å 및 O-Tl-O=92.33(4)°). 약 4개의 Tl^+ 이온은 세 개의 산소로 만들어지는 평면으로부터 소다라이트 동공쪽으로 1.695 Å 떨어진 자리 II에 위치해 있다(Tl-O=2.81 (1) Å 및 O-Tl-O=87.48(3)°). 나머지 26개의 Tl^+ 이온들은 자리 III'에 분포된다(Tl-O=2.82 (1) Å 및 Tl-O=2.88(3) Å). $Ca_{32}Tl_{28}$-X 결정 구조에서는 16개의 Ca^{2+} 이온과 15개의 Tl^+ 이온들이 자리 II를 점유하고 있다(Ca-O=2.26(1) Å 및 O-Ca-O=119.14(4)°; Tl-O=2.70(1) Å 및 O-Tl-O=92.38°). 한 개의 Tl^+ 이온들은 자리 II를 점유한다. 나머지 12개의 Tl^+ 이온들은 자리III'에 분포된다.

ABSTRACT. Two anhydrous crystal structures of fully dehydrated, Ca^{2+}- and Tl^+-exchanged zeolite X, $Ca_{18}Tl_{56}Si_{100}Al_{92}O_{384}$ ($Ca_{18}Tl_{56}$-X; a=24.883(4) Å) and $Ca_{32}Tl_{28}Si_{100}Al_{92}O_{384}$ ($Ca_{32}Tl_{28}$-X; a=24.973(4) Å) per unit cell, have been determined by single-crystal X-ray diffraction techniques in the cubic space group $Fd\bar{3}$ at 21(1) °C. $Ca_{18}Tl_{56}$-X was prepared by ion exchange in a flowing stream of 0.045 M aqueous $Ca(NO_3)_2$ and 0.005 M $TlNO_3$. $Ca_{32}Tl_{28}$-X was prepared similarly using a mixed solution of 0.0495 M $Ca(NO_3)_2$ and 0.0005 M $TlNO_3$. Each crystal was then dehydrated at 360 °C and 2×10^{-6} Torr for 2 days. Their structures were refined to the final error indices, R_1=0.039 and R_2=0.036 with 382 reflections for $Ca_{18}Tl_{56}$-X , and R_1=0.046 and R_2=0.045 with 472 reflections for $Ca_{32}Tl_{28}$-X for which $I>3\sigma(I)$. In the structures of dehydrated $Ca_{18}Tl_{56}$-X and $Ca_{32}Tl_{28}$-X, Ca^{2+} and Tl^+ ions are located at six crystallographic sites. Sixteen Ca^{2+} ions fill the octahedral sites

I at the centers of double six rings ($Ca_{18}Tl_{56}$-X : Ca-O=2.42(1) and O-Ca-O=93.06(4)°; $Ca_{32}Tl_{28}$-X : Ca-O=2.40(1) Å and O-Ca-O=93.08(3)°). In the structure of $Ca_{18}Tl_{56}$-X, another two Ca^{2+} ions occupy site II (Ca-O=2.35(2) Å and O-Ca-O=111.69(2)°) and twenty six Tl^+ ions occupy site II opposite single six-rings in the supercage; each is 1.493 Å from the plane of three oxygens (Tl-O=2.70(8) Å and O-Tl-O=92.33(4)°). About four Tl^+ ions are found at site II', 1.695 Å into sodalite cavity from their three oxygen plane (Tl-O=2.81 (1) and O-Tl-O=87.48(3)). The remaining twenty six Tl^+ ions are distributed over site III' (Tl-O=2.82 (1) Å and Tl-O=2.88(3)°). In the structure of $Ca_{32}Tl_{28}$-X, sixteen Ca^{2+} ions and fifteen Tl^+ ions occupy site III' (Ca-O=2.26(1) Å and O-Ca-O=119.14(4)°; Tl-O=2.70(1) Å and O-Tl-O=92.38°) and one Tl^+ ion occupies site II'. The remaining twelve Tl^+ ions are distributed over site III'. It appears that Ca^{2+} ions prefer sites I and II in that order and Tl^+ ions occupy the remaining sites.

INTRODUCTION

Zeolites are materials with unique properties which find uses in such diverse fields as oil cracking, nuclear waste treatment, and animal feed supplementation.[1] Especially, zeolites have been the subject of numerous investigations because of their importance in adsorption and catalysis. Most efforts have been placed into zeolite modification whereby the introduction of cations, usually by ion exchange, has been used to modify the catalytic or molecular sieving actions of the parent zeolite.

The catalytic properties of transition metal ion exchanged zeolites are well-known. A variety of structures have been studied over transition metal ion exchanged zeolites.[2-10] Smolin, Shepelev, and Anderson studied the crystal structures of hydrated and dehydrated Ca^{2+}-exchanged zeolite X.[2] In the initial hydrated form, Ca^{2+} ions are located in the sodalite cavities and supercages. Upon dehydration, the Ca^{2+} ions migrate into D6R and to sites in the single six- oxygen rings.

Recently the structures of Cd_{46}-X[3], Ca_{46}-X[4], Mg_{46}-X[4], Ba_{46}-X[5], K_{92}-X[6] and Tl_{92}-X[7] were determined by using single-crystal X-ray diffraction techniques. These cations generally occupy site I preferentially except for the largest and the smallest. Ca^{2+} ions in Ca_{46}-X[4] and K^+ ions in K_{92}-X[6] fully occupy site I position but only 13 Ba^{2+} ions (relatively large) in Ba_{46}-X[5] and and 14 Mg^{2+} ions (relatively small) in Mg_{46}-X[4] occupy the 16-fold site I positions. In Tl_{92}-X[7], Tl^+ ions are found at four different crystallographic sites. Tl^+ ions do not occupy site I; that remains empty. Also, several structural studies of mixed cation system of mono- and divalent ion exchanged

zeolite A and X have been reported.[3-7] These works have been performed to study the site selectivity of various cations.

In our recent work, $Ca_{32}K_{28}$-X[8], $Ca_{31}Rb_{30}$-X[9], $Cd_{24.5}Tl_{43}$-X[3], $Sr_{31}K_{30}$-X[10] and $Sr_{8.5}Tl_{75}$-X[10] have been determined.[3-10] In these structure, 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 Tl^+ and K^+ ions, which are less able to balance the anionic charge of the zeolite framework because of their size, finish satisfying the double six ring with some occupancy at I', and finish filling site II, with the remainder going to site III, the least suitable cation site in the structure.

In this work, the occupancy numbers and locations of cations in the structure of dehydrated $Ca_{18}Tl_{56}$-X are compared with those of dehydrated $Ca_{32}Tl_{28}$-X. We would also learn the relative preference of the cation for the coordination sites available within the zeolite. It is easy to distinguish between Ca^{2+} and Tl^+ because of the large difference in their atomic scattering factors ($80e^-$ for Tl^+ and $18e^-$ of Ca^{2+}) and ionic radii (Tl^+=1.47 Å and Ca^{2+}=0.99 Å).

EXPERIMENTAL SECTION

Large single crystals of sodium zeolite X with stoichiometry $Na_{92}Si_{100}Al_{92}O_{384}$ were prepared in St. Petersburg, Russia.[11] One of these, a colorless octahedron about 0.2 mm in cross-section, was lodged in a fine Pyrex capillary.

$Ca_{18}Tl_{56}$-X (crystal 1) and $Ca_{32}Tl_{28}$-X (crystal 2) were prepared using exchange solutions whose $Ca(NO_3)_2$:

TlNO₃ mole ratios were 10 : 1 and 100 : 1, respectively, with a total concentration of 0.05 M. The solution was allowed to flow past the crystal at a velocity of approximately 15 mm/s for 4 d at 21(1) °C. After dehydration at 360 °C and 2×10^{-6} Torr for 2 d, both crystals were yellow. After cooling to room temperature, each crystal, still under vacuum, was sealed in its capillary by torch. Subsequent diffraction experiments were performed at 21(1) °C.

The cubic 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 lacks that mirror plane. Diffraction data were collected with an automated Enraf-Nonius fourcircle computercontrolled CAD-4 diffractometer equipped with a pulseheight analyzer and graphite monochromator, using Mo radiation ($K\alpha_1$, λ=0.70930; $K\alpha_2$, =0.71359 Å). The cubic unit cell constant at 21(1) °C, determined by least-squares refinement of 25 intense reflections for which $14° < 2\theta < 22°$, are a=24.988(4) Å for $Ca_{18}Tl_{56}$-X and 24.973(4) Å for $Ca_{32}Tl_{28}$-X. All unique reflections in the positive octant of an F-centered unit cell for which $2\theta < 50°$, $l > h$, and $k > h$ were recorded. Of the 1392 unique reflections measured for $Ca_{18}Tl_{56}$-X and 1386 for $Ca_{32}Tl_{28}$-X, only the 382 and 472 reflections, respectively, for which $I > 3\sigma(I)$ were used in subsequent structure determination. An absorption correction (μR=0.080, ρ_{cal} =1.680 g/cm³ and $F(000)$= 7288)[12] was made empirically using a ψ scan. 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 previously reported.[13]

STRUCTURE DETERMINATION

$Ca_{18}Tl_{56}$-X (crystal 1). 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 Ca_{46}-X.[4] Anisotropic refinement converged to an unweighted R_1 index, $(\Sigma F_o-|F_c|)/\Sigma F_o)$, of 0.57 and a weighted R_2 index, $(\Sigma w(F_o-|F_c|)^2/\Sigma wF_o^2)^{1/2}$, of 0.63.

A difference Fourier function revealed two large peaks at (0.255, 0.255, 0.255) and (0.0, 0.0, 0.0) with heights of 9.0 eÅ⁻³ and 10.5 eÅ⁻³, respectively. Anisotropic refinement including these as Tl⁺ ion at Tl(1) and Ca²⁺ ion at Ca(1) converged to R_1=0.213 and R_2=0.317 with occupancies of 16.7(6) and 26.3(1), respectively. These values were reset and fixed at 16 Ca²⁺ and 26 Tl⁺ ions, respectively.

It is not difficult to distinguish Ca²⁺ from Tl⁺ ion for several reasons. First, their atomic scattering factors are quite different, 18e⁻ for Ca²⁺ and 80e⁻ for Tl⁺. Secondly, their ionic radii are different, Ca²⁺=0.99 Å and Tl⁺=1.47 Å.[22] Also, the approach distances between those ions and zeolite oxygens in dehydrated Tl_{12}-A[14] and Ca_6-A[15] have been determined and are indicative. Finally, the requirement that the cationic charge sum to +92 per unit cell does not allow the major positions to refine to acceptable occupancies with an alternating assignment of ionic identities.

A subsequent difference Fourier synthesis revealed a peak at Tl(3), (0.178, 0.178, 0.178) of height 11.6 eÅ⁻³. Anisotropic refinement of the framework atoms, Ca(1), Tl(1), Tl(3) (see *Table* 1) converged to R_1=0.19 and R_2=0.23.

A subsequent difference Fourier synthesis showed a peak at Ca(2), (0.24, 0.24, 0.24), with a peak height 7.1 eÅ⁻³ and a peak at Tl(2), (0.41, 0.10, 0.12), with a peak height 5.3 eÅ⁻³. Anisotropic refinement of the framework atoms, Ca(2), and Tl(2) converged to R_1=0.053 and R_2=0.058. From successive difference Fouriers, one peak was found at (0.41, 0.08, 0.08) with a height 2.5 eÅ⁻³ and refined Tl⁺ ions at Tl(4). Anisotropic refinement of framework atoms and all the cations converged to R_1 = 0.038 and R_2 = 0.035. The occupancies of Ca(2), Tl(2), Tl(3), and Tl(4) were fixed at the values shown in the *Table* 1 considering the cationic charge per unit cell. The sum of occupancy numbers at Ca(2), Tl(1), and Tl(3) were fixed at 32.0, the maximum number of ions per unit cell at these positions. The final error indices for the 382 reflections for which $I > 3\sigma(I)$ were R_1=0.039 and R_2=0.036. The shift in the final cycle of least-squares refinement were less than 0.1% of their corresponding standard deviations. Atomic scattering factors[16,17] for Si, Al, O⁻, Ca²⁺, and Tl⁺ were used. All scattering factors were modified to account for anomalous dispersion.[18]

Table 1. Positional, thermal, and occupancy parameters[a] for dehydrated Ca$_{18}$Tl$_{56}$-X

Atom	Wyc. Pos.	x	y	z	[b]U_{11} or [d]U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	[c]Occupancy varied	[c]Occupancy fixed
Si	96(g)	−538(2)	342(2)	1230(2)	83(19)	59(20)	80(19)	22(21)	−14(23)	29(25)		96
Al	96(g)	−543(2)	1224(2)	360(2)	82(22)	40(20)	48(24)	12(24)	−3(22)	−55(25)		96
O(1)	96(g)	−1076(4)	−2(6)	1105(4)	161(55)	373(65)	120(56)	−92(80)	−35(44)	−26(81)		96
O(2)	96(g)	−47(5)	−40(5)	1437(3)	162(49)	161(48)	139(43)	73(67)	−4(65)	79(65)		96
O(3)	96(g)	−359(5)	622(5)	655(4)	260(67)	154(65)	−10(56)	−35(64)	23(58)	−17(48)		96
O(4)	96(g)	−664(5)	795(5)	1676(5)	244(70)	168(65)	98(62)	18(64)	18(64)	−54(53)		96
Ca(1)	16(c)	0	0	0	79(12)	79(12)	79(12)	10(30)	10(30)	10(30)	16.7(2)	16
Ca(2)	32(e)	2336(23)	2336(23)	2336(23)	213(297)[d]						1.51(4)	2
Tl(1)	32(e)	2521(0)	2521(0)	2521(0)	221(2)	221(2)	221(2)	−37(7)	−37(7)	−37(7)	26.3(1)	26
Tl(2)	96(g)	4114(1)	1109(2)	1353(3)	177(17)	824(54)	1448(54)	−141(22)	236(30)	−16(35)	22.3(2)	22
Tl(3)	32(e)	1781(3)	1781(3)	1781(3)	151(23)	151(23)	151(23)	37(27)	37(27)	37(27)	4.1(1)	4
Tl(4)	96(g)	4182(11)	830(12)	865(12)	623(60)[d]						5.1(2)	4

[a] $a=25.200(3)$ Å, space group $Fd\bar{3}$ origin at center of symmetry. Positional 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. [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. [d] $U_{iso}=(B_{iso}/8\pi^2)$

Table 2. Positional, thermal, and occupancy parameters[a] for dehydrated Ca$_{32}$Tl$_{28}$-X

Atom	Wyc. Pos.	x	Y	z	[b]U_{11} or [d]U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	[c]Occupancy varied	[c]Occupancy fixed
Si	96(g)	−542(2)	338(2)	1229(19)	141(19)	93(19)	84(18)	−10(21)	−35(28)	−19(24)		96
Al	96(g)	−554(2)	1220(2)	365(2)	119(20)	78(20)	98(21)	10(29)	11(22)	−23(26)		96
O(1)	96(g)	−1077(4)	−0(6)	1122(4)	177(53)	176(48)	153(59)	−38(70)	91(42)	−112(73)		96
O(2)	96(g)	−47(5)	−39(5)	1435(3)	124(44)	93(41)	198(46)	100(57)	−62(60)	−71(63)		96
O(3)	96(g)	−354(4)	609(4)	651(4)	110(51)	58(53)	124(59)	64(54)	−11(54)	8(48)		96
O(4)	96(g)	−637(4)	772(5)	1675(4)	385(73)	198(62)	95(56)	−31(67)	152(68)	−90(51)		96
Ca(1)	16(c)	0	0	0	80(13)	80(13)	80(13)	20(29)	20(29)	20(29)	16.5(3)	16
Ca(2)	32(e)	2227(4)	2227(4)	2227(4)	338(34)	338(34)	338(34)	190(46)	190(46)	190(46)	15.8(4)	16
Tl(1)	32(e)	2518(1)	2518(1)	2518(1)	251(4)	251(4)	251(4)	−44(12)	−44(12)	−44(12)	15.7(5)	15
Tl(2)	96(g)	4098(4f)	1195(12)	1373(5)	56(40)	2227(178)	534(132)	20(139)	139(58)	23(118)	6.7(12)	7
Tl(3)	32(e)	1813(10)	1813(10)	1813(10)	577(109)[d]						0.5(6)	1
Tl(4)	96(g)	4182(11)	750(7)	750(7)	1064(77)[d]						5.3(2)	5

[a] $a=25.200(3)$ Å, space group $Fd\bar{3}$ origin at center of symmetry. Positional 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. [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. [d] $U_{iso}=(B_{iso}/8\pi^2)$

The final structural parameters and selected interatomic distances and angles are presented in *Tables* 1 and 3.

Ca$_{32}$Tl$_{28}$-X (crystal 2). Full-matrix least-squares refinement was initiated by using the atomic parameters of the framework atoms for the previous crystal of Ca$_{18}$Tl$_{56}$-X (crystal 1). Anisotropic refinement converged to an unweighted R_1=0.47 and a weighted R_2=0.53. A difference Fourier function revealed two large peaks at

(0.0, 0.0, 0.0) with a height 16.93 eÅ^{-3} and (0.253, 0.253, 0.253) with a height 11.3 eÅ^{-3}. Anisotropic refinement including these as Ca^{2+} ions at Ca(1) and Tl$^+$ ions at Tl(1) converged to R_1=0.177 and R_2=0.212 with occupancies of 13.7(9) at Ca(1) and 14.4(2) at Tl(2).

A subsequent difference Fourier function revealed two additional peaks, at (0.2201, 0.2201, 0.2201) with a height 7.19 eÅ^{-3}, and at (0.08, 0.08, 0.08) with a height

Table 3. Selected interatomic distance (Å) and angles (deg)

	$Ca_{18}Tl_{56}$-X	$Ca_{32}Tl_{28}$-X
Si-O(1)	1.62(1)	1.60(1)
Si-O(2)	1.63(1)	1.64(1)
Si-O(3)	1.66(1)	1.66(1)
Si-O(4)	1.61(1)	1.58(1)
Mean	1.63	1.62
Al-O(1)	1.70(1)	1.72(1)
Al-O(2)	1.69(1)	1.74(1)
Al-O(3)	1.73(1)	1.76(1)
Al-O(4)	1.69(1)	1.73(1)
Mean	1.70	1.74
Ca(1)-O(3)	2.42(1)	2.40(1)
Ca(2)-O(2)	2.35(2)	2.26(1)
Tl(1)-O(2)	2.70(8)	2.70(1)
Tl(2)-O(4)	2.82(1)	2.87(2)
Tl(3)-O(2)	2.81(1)	2.82(3)
Tl(4)-O(1)	2.88(3)	2.88(2)
O(1)-Si-O(2)	111.9(7)	112.7(6)
O(1)-Si-O(3)	106.2(6)	107.7(5)
O(1)-Si-O(4)	110.1(6)	110.5(5)
O(2)-Si-O(3)	108.4(6)	107.4(5)
O(2)-Si-O(4)	109.6(6)	105.9(5)
O(3)-Si-O(4)	110.7(6)	112.7(5)
O(1)-Al-O(2)	111.4(7)	111.7(6)
O(1)-Al-O(3)	104.7(6)	105.8(5)
O(1)-Al-O(4)	111.4(6)	113.6(5)
O(2)-Al-O(3)	109.2(6)	107.8(5)
O(2)-Al-O(4)	108.48(6)	104.0(5)
O(3)-Al-O(4)	111.7(6)	113.9(5)
Si-O(1)-Al	128.0(7)	126.1(6)
Si-O(2)-Al	141.1(6)	139.9(6)
Si-O(3)-Al	131.3(7)	129.3(6)
Si-O(4)-Al	158.6(8)	163.3(7)
O(3)-Ca(1)-O(3)	89.94(4)	87.10(3)
O(2)-Ca(2)-O(2)	93.06(4)	93.08(3)
	111.69(2)	119.14(4)
O(2)-Tl(1)-O(2)	92.33(4)	92.38(34)
O(4)-Tl(2)-O(4)	65.68(3)	67.84(35)
O(2)-Tl(3)-O(2)	87.48(3)	87.10(44)
O(1)-Tl(4)-O(1)	115.78(10)	111.81(57)
O(1)-Tl(4)-O(4)	60.4(7)	63.07(45)

Numbers in parentheses are estimated standard deviations in least significant digit for the corresponding Values

3.14 eÅ^{-3}. Calculations including these peaks as ions at Ca(2) and Tl(4) lowered the error indices to R_1=0.084 and R_2=0.092. The occupancy numbers at Ca(2) and Tl(4) were refined to 14.5(6) and 7.9(3), respectively. From an ensuring Fourier function, the remaining Tl$^+$ ion positions were found at (0.40, 0.12, 0.14) with height 3.73 eÅ^{-3} and at (0.178, 0.178, 0.178) with a height 2.89 eÅ^{-3}.

Anisotropic refinement of framework atoms and all the cations converged to R_1=0.045 and R_2=0.043. The occupancies of Ca(1), Ca(2), Tl(1), Tl(2), Tl(3), and Tl(4) were fixed at the values shown in the *Table* 2 considering the cationic charge per unit cell. The sum of occupancy numbers at Ca(2), Tl(1), and Tl(3) were fixed at 32.0, the maximum number of ions per unit cell at these positions. Otherwise the final error indices for the 472 reflections for which $I > 3\sigma(I)$ were R_1=0.046 and R_2=0.045. The shift in the final cycle of least-squares refinement were less than 0.1% of their corresponding standard deviations. All crystallographic calculations were done using MolEN[19] (a structure determination program package supplied by Enraf-Nonius). Atomic scattering factors[16,17] for Si, Al, O$^-$, Ca^{2+}, and Tl$^+$ were used. All scattering factors were modified to account for anomalous dispersion.[18] The final structural parameters are listed in *Table* 2 and selected interatomic distances and angles are presented in *Table* 3.

DISCUSSION

Zeolite X is a synthetic counterpart of the naturally occurring mineral faujasite. 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 the zeolite (see *Fig.* 1). These -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
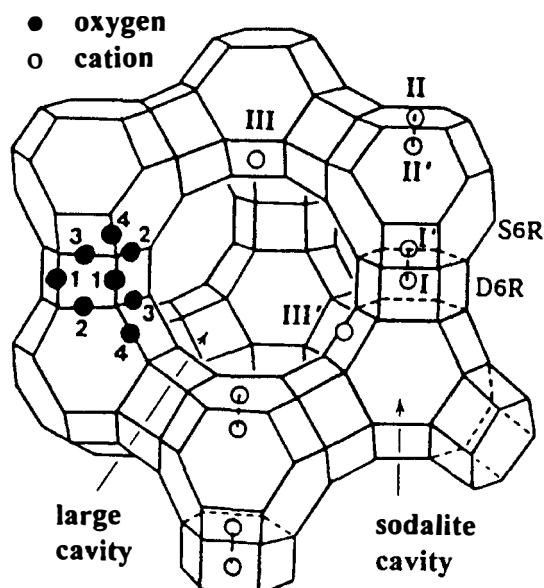
- ● oxygen
- ○ cation

Fig. 1. A stylized draws 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 to 4. Silicon and aluminum atoms alternate at the tetrahedral intersections, except that a silicon atom substitutes for aluminum at about 4% of the Al positions. Extraframework cation positions are labeled with Roman numerals

Fig. 2. Stereoview of a sodalite cavity with an attached D6R in dehydrated Ca₁₈Tl₅₆-X. One Ca²⁺ ion at Ca(1) (site I) and three Tl⁺ ions at Tl(1) (site II) and one Ca²⁺ ion at Ca(2) (site II) are shown. About 25% of sodalite cavities may have this arrangement. Ellipsoids of 20% probability are shown

Fig. 3. Stereoview of a sodalite cavity with an attached D6R in dehydrated Ca₁₈Tl₅₆-X. One Ca²⁺ ion at Ca(1) (site I) and three Tl⁺ ions at Tl(1) (site II) and one Tl⁺ ion at Tl(3) (site II') are shown. About 50% of sodalite cavities may have this arrangement. The remaining of 20% of sodalite cavities may have 4Tl⁺ ions at Tl(1). Ellipsoids of 20% probability are shown

zeolite's cavities. They are usually found at the following sites shown in *Fig.* 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.[20,21]

Ca₁₈Tl₅₆-X (crystal 1). The mean values of the Si-O and Al-O bond lengths are 1.63 and 1.70 Å, respectively. The individual bond lengths, however, show marked variations: Si-O from 1.61(1) to 1.66(1) Å and Al-O from 1.69(1) to 1.73(1) Å. The Si-O and Al-O distances depend on Ca²⁺ ion coordination to framework oxygen; Ca²⁺ ions coordinate only to O(2) and O(3). As a consequence of these (substantially ionic) interactions, the Si-O(2), Si-O(3), Al-O(2), and Al-O(3) bonds are somewhat lengthened (see Table 3). This effect is frequently observed, for example, in dehydrated Ca₄₆-X.[4]

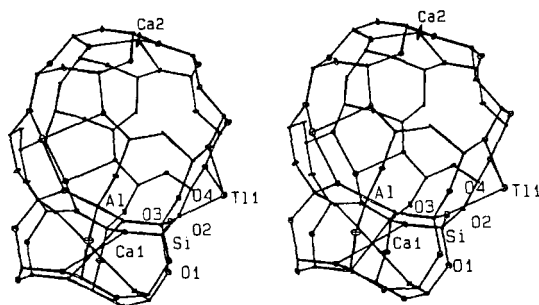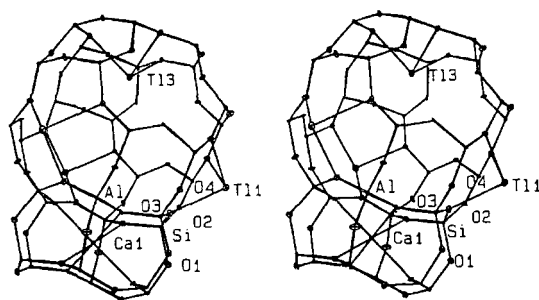In this structure, 18 Ca²⁺ ions occupy two crystallo-graphic sites and 56 Tl⁺ ions occupy four sites. The Ca²⁺ ions at Ca(1) fill the 16-fold site I. Sixteen Ca²⁺ ions at Ca(1) fill the octahedral site I, at the centers of the D6R's (see *Figs.* 2 and 3). The Ca(1)-O(3) distance, 2.42(1) Å, is a little longer than the sum of the ionic radii of Ca²⁺ and O²⁻, 0.99 + 1.32=2.31 Å,[22] indicating a reasonably good fit. In dehydrated Ca₄₆-X, the Ca(1)-O(3) distance is similar, 2.429(8) Å.[4] The remaining two Ca²⁺ ions at Ca(2) are at site II in the supercage (see *Figs.* 3 and 5); these Ca²⁺ ions are 2.35(2) Å from their nearest neighbors, three O(2) framework oxygens. About 26 Tl⁺ ions at Tl(1) occupy the 32-fold site II supercage. Tl(1)-O(2) is 2,70(8) Å, which is a little shorter than the sum of the ionic radii of Tl⁺ and O²⁻, 1.47+1.32=2.79 Å,[22] and each Tl(1) ion is 1.49 Å from the plane of the three O(2)

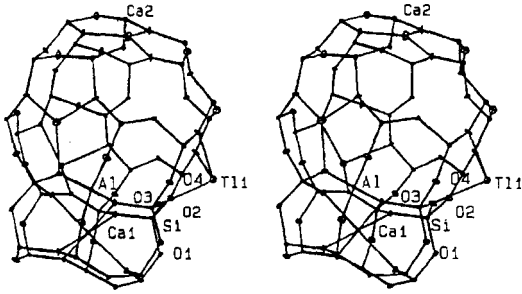*Fig.* 4. Stereoview of a sodalite cavity with an attached D6R in dehydrated Ca₃₂Tl₂₈-X. One Ca²⁺ ion at Ca(1) (site I) and two Ca²⁺ ions at Ca(2) (site II) and two Tl⁺ ions at Tl(1) (site II) are shown. About 87.5% of sodalite cavities may have this arrangement. Ellipsoids of 20% probability are shown.
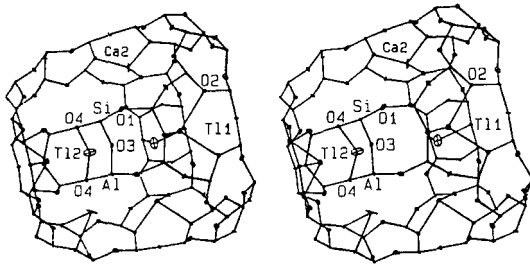

Fig. 5. Stereoview of the supercage of dehydrated Ca₁₈Tl₅₆-X. Three Tl⁺ ions at ions at Tl(1) (site II) and one Ca²⁺ ion at Ca(2) (site II) and three Tl⁺ ions at Tl(2) (site III') are shown. About 25% supercages may have this arrange ment. Ellipsoids of 20% probability are used.

framework oxygens of the S6R to which it is bound (O(2)-Tl-O(2)=92.33(4)°).

The Tl(2)-O(4) bonds occupy site III' in the supercage with occupancies of 22 and 4, respectively. Twenty two Tl⁺ ions at Tl(2) occupy the 96-fold position (Tl(2)-O(4)=2.82(1) Å) This distance is similar to Tl-O distances in dehydrated Sr₈.₅Tl₇₅-X[10] and Cd₂₄.₅Tl₄₃-X[3] (2.86(2) Å and 2.79(2) Å). The four Tl⁺ ions at Tl(4) lie in the supercage at site III'.

The remaining four Tl⁺ ions at Tl(3) occupy the 32-fold position at site II' (see *Figs.* 3 and 6). The Tl(3)-O(2) approach distance, 2.81(1) Å, is nearly the same as the sum of the ionic radii of Tl⁺ and O²⁻, 1.47 Å + 1.32 Å.

Recently the structures of Cd₄₆-X[3], Ca₄₆-X[4], Cd₂₄.₅Tl₄₃-X[3], and Ca₃₂K₂₈-X[8] were determined. From these it appears that site I is the lowest energy site for most cations, except for the largest and the smallest. Ca²⁺ ions in Ca₄₆-X[4] and Cd²⁺ ions in Cd₄₆-X[3] fill site I, with the
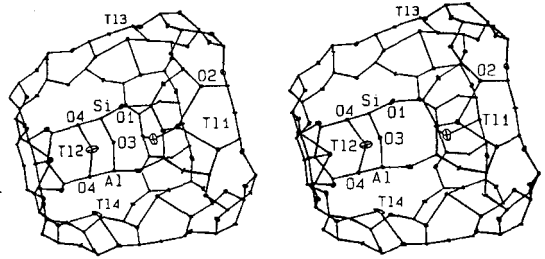
Fig. 6. Stereoview of the supercage of dehydrated Ca₁₈Tl₅₆-X. Three Tl⁺ ions at ions at Tl(1) (site II) and two Tl⁺ ions Tl(2) (site III') and one Tl⁺ ion at Tl(3) (site II') and one Tl⁺ ion at Tl(4) (site III') are shown. About 25% supercages may have this arrangement. Ellipsoids of 20% probability are used.

remainder going to site II in the supercage, nearly filling it. In Cd₂₄.₅Tl₄₃-X, ion size and charge dominate the competition for sites. The smaller and more highly charged Cd²⁺ ions select their sites first because they can access more closely to anionic oxygens of the zeolite framework. They nearly fill the site I position as in Cd₄₆-X, ascertaining that Cd²⁺ ions prefer site I, the D6R sites. Only after the Cd²⁺ ions have selected their sites, the Tl⁺ ions finish filling site II, with the remainder going to the least suitable cation site in the structure, site III.

Ca₃₂Tl₂₈-X (crystal 2). In this structure, 32 Ca²⁺ ions occupy two crystallographic sites and 28 Tl⁺ ions occupy four sites. The Ca²⁺ ions at Ca(1) lie at site I. Sixteen Ca²⁺ ions at Ca(1) fill the octahedral site I at the centers of the D6R's (see *Fig.* 4) (Ca(1)-O(3)=2.40(1) Å and O(3)-Ca(1)-O(3)=90.08(3)° and 87.10(3)°). Another 16 Ca²⁺ ions at Ca(2) occupy 32-fold site II in the supercage (see *Figs.* 7 and 8): The Ca(2)-O(2) distance, 2.26 Å, is
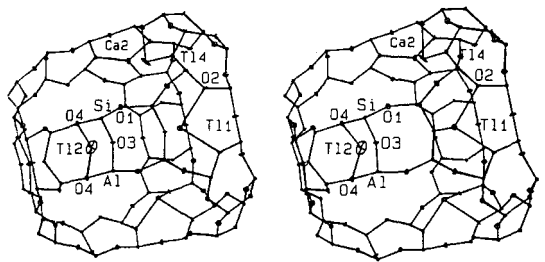

Fig. 7. Stereoview of the supercage of dehydrated Ca₃₂Tl₂₈-X. Two Ca²⁺ ions at Ca(2) (site II) and two Tl⁺ ions Tl(1) (site II) and one Tl⁺ ion at Tl(2) (site III') and one Tl⁺ ion at Tl(4) (site III') are shown. About 50% supercages may have this arrangement. Ellipsoids of 20% probability are used
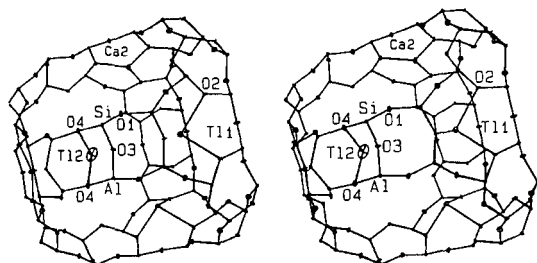
Fig. 8. Stereoview of the supercage of dehydrated $Ca_{32}Tl_{28}$-X. Two Ca^{2+} ions at Ca(2) (site II) and two l^+ ions Tl(1) (site II) and one Tl^+ ion at Tl(2) (site III') are shown. About 37.5% of the supercages may have this arrangement. Ellipsoids of 20% probability are used.

Table 4. Deviations (Å) of cations from six-ring planes

	$Ca_{18}Tl_{56}$-X	$Ca_{32}Tl_{28}$-X
At O(3)[a]		
Ca(1)	−1.32(1)	−1.31(1)
At O(2)[b]		
Ca(2)	0.69(3)	0.23(1)
Tl(1)	1.49(1)	1.48(1)
Tl(2)	0.07(1)	0.20(1)
Tl(3)	−1.69(1)	−1.61(2)

[a]A negative deviation indicates that the atom lies in a D6R. [b]A positive deviation indicates that the atom lies in the supercage and a negative deviation indicates that the atom lies in the sodalite cavity.

shorter than the sum of the conventional radii[22] of Ca^{2+} and O^{2-}, 2.31 Å, presumably because Ca(2) is only three-coordinate. These Ca^{2+} ions are slightly recessed, 0.23 Å into the supercage from the plane of the three O(2) oxygens. (see Table 3 and 4). The O(2)-Ca(2)-O(2) bond angle, 119.1(4)°, is nearly trigonal planar. The Tl(1) position is at site II, far inside the supercage . Each Tl(1) ion is 1.48 Å from the plane of the three O(2) framework oxygens of the S6R to which it is bound. The Tl(1)-O(2) distances are 2.70(1) Å. In dehydrated $Sr_{1.6}Tl_{8.8}$-A[23] and Tl_{12}-A[14], similar Tl-O distances (2.66(1) Å and 2.62(1) Å) and Tl^+ displacements from six-ring planes (1.51 Å and 1.56 Å) have also been observed. The Tl^+ ions at Tl(2) lie in the supercage at site III'. About seven Tl^+ ions at Tl(2) occupy 96-fold position and the five Tl^+ ions at Tl(4) lie in the supercage at site III'. The Tl(3) position is at site II', on a threefold axis inside the sodalite unit at the single six-oxygen ring. This is 32-fold position, but it is occupied by only one Tl^+ ion. The Tl(3)-O(2)

Table 5. Distribution of nonframework atoms over sites

Sites \ Crystals	$Ca_{18}Tl_{56}$-X	$Ca_{32}Tl_{28}$-X
I	16Ca(1)	16Ca(1)
II'	4Tl(3)	1Tl(3)
II	2Ca(2)	16Ca(2)
	26Tl(1)	15Tl(1)
III'	22Tl(2)	7Tl(2)
	4Tl(4)	5Tl(4)

distances are 2.82(3) Å, similar to the sum of the corresponding ionic radii, 1.47+1.32=2.79 Å[22].

CONCLUSION

This work indicates not only that all of Na^+ ions in zeolite X can readily be replaced by Tl^+ and Ca^{2+} ions but also that full dehydration to yield relatively simple structures is possible.

Table 5 shows that there was no competition for site I in $Ca_{18}Tl_{56}$-X and $Ca_{32}Tl_{28}$-X but there was only competition for site II. This is the reason that Tl^+ ions are too large to occupy site I. This is not a kinetic or sieving effect; because Tl^+ ions are found in the sodalite units of zeolite A[24,25], they must have entered through 6-rings. Therefore Ca^{2+} ions nearly fill site I without competition and the remainder going to the site II as in $Ca_{18}Tl_{56}$-X and $Ca_{32}Tl_{28}$-X. The size and charge of ions appear to control the competition for site II. The smaller and more highly charged Ca^{2+} ions preferentially occupy site II and larger Tl^+ ions are less able to balance anionic charge of the zeolite framework because of their size.

Supporting Information Available. Tables of calculated and observed structure factors (11 pages). Ordering information is given on any current masthead page.

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