Two Crystal Structures of Ag$^+$-and Tl$^+$-Exchanged Zeolite X, Ag$_{27}$Tl$_{65}$-X and Ag$_{23}$Tl$_{69}$-X

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Two crystal structures of dehydrated Ag$^+$- and Tl$^-$-exchanged zeolite X (Ag$_{27}$Tl$_{65}$-X and Ag$_{23}$Tl$_{69}$-X) have been determined by single-crystal X-ray diffraction techniques in the cubic space group $Fd\bar{3}$ at 21(1) °C (a = 24.758(4) Å, a = 24.947(4) Å, respectively). Their structures were refined to the final error indices R_1 = 0.055 and wR_2 = 0.057 with 375 reflections, and R_1 = 0.058 and wR_2 = 0.057 with 235 reflections, respectively, for which $I > 3\sigma(I)$. In the structure of Ag$_{27}$Tl$_{65}$-X, 27 Ag$^-$ ions were found at two crystallographic sites: 15 Ag$^+$ ions at site I at the center of the hexagonal prism and the remaining 12 Ag$^+$ ions at site II' in the sodalite cavity. Sixty-five Tl$^-$ ions were located at three crystallographic sites: 20 Tl$^+$ ions at site II opposite single six-rings in the supercage. 18 Tl$^+$ ions at site I' in the sodalite cavity opposite the D6Rs, and the remaining 27 Tl$^+$ ions at site III' in the supercage. In the structure of Ag$_{23}$Tl$_{69}$-X, 23 Ag$^+$ ions were found at two crystallographic sites: 15 at site I and 8 at site II'. Sixty-nine Tl$^-$ ions are found at four crystallographic sites: 24 at site II, 17 at site I', and the remaining 28 at two III' sites with occupancies of 22 and 6.

Key Words : Zeolite X, Structure. Silver, Thallium

Introduction

Synthetic zeolite X has the same framework structure as 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 the physical and chemical properties of zeolites. So, the problem of the reactivity and location of the exchanged ions is of interest from both theoretical and practical points of view.

Zeolite X has a wide range of industrial applications primarily due to the excellent stability of the crystal structure and the large available pore volume and surface area.[5] In addition to the accessible pore volume. the sorptive and catalytic properties of zeolites heavily depend on the size. charge density. and distribution of cations in the lattice. Alkali-metal cation-exchanged zeolites have been the subject of numerous investigations because of their importance in adsorption and catalysis. The introduction of transition metals into zeolites induces new catalytic activity.[6] They can coordinate with guest molecules more selectively than filled-shell cations and often reach other oxidation states easily.

Kim *et al.* studied the crystal structure of dehydrated Tl$^+$-exchanged zeolite X.[7] In Tl$_{92}$-X. 92 Tl$^+$ ions are found at four different crystallographic sites: I' in the sodalite cavity

on a three-fold axis. II in the supercage. and two crystallographically different III' sites. Tl$^+$ ions are too large to occupy site I. the center of the double six-ring.

Several structural studies of monovalent and divalent ion-exchanged zeolites A and X have been reported observing the site selectivity of various cations.[8-12] The structures of fully dehydrated Ca$_{32}$K$_{28}$-X,[8] Ca$_{31}$Rb$_{30}$-X,[9] Cd$_{24.5}$Tl$_{43}$-X,[10] Sr$_{31}$K$_{30}$-X,[11] Sr$_{8.5}$Tl$_{75}$-X,[11] Ni$_{17}$Tl$_{58}$-X[12] and Ni$_{12}$Tl$_{68}$-X[12] were determined. In these structures. the small and highly charged Cd^{2+}, Ca^{2+}, and Sr^{2+} ions tend to occupy site I. with the remainder going to site II. The large Tl$^+$ and K$^+$ ions. which are less able to balance the anionic charge of the zeolite framework than the small and highly charged divalent ions. can fill the double six-ring with some occupancies at site I' and finish filling site II. with the remainder of them going to the least suitable cationic sites in the structure. sites III and III'.

The present work was done to study the site selectivity of cations in fully dehydrated Ag$^-$- and Tl$^+$-exchanged zeolite X. As the structural stability and catalytic property of zeolites depend on the type and number of cations and their distribution over the available sites. it is meaningful to determine the cationic positions and occupancies in the zeolite framework.

Experimental Section

Large single crystals of zeolite Na-X. stoichiometry Na$_{92}$-Si$_{100}$Al$_{92}$O$_{384}$. were prepared by Bogomolov and Petranovskii in St. Petersburg. Russia.[13] Two of these. colorless octahedra about 0.2 mm in cross-section. were lodged in two fine Pyrex capillaries.

Ag$_{27}$Tl$_{65}$-X and Ag$_{23}$Tl$_{69}$-X were prepared by using an

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exchange solution that had a $AgNO_3$: $TlNO_3$ mole ratio of 1 : 5 and 1 : 10, respectively, with a total concentration of 0.05 M. The solution was allowed to flow past each crystal for 3 days. The colorless crystals were dehydrated at 400 °C for 2 days in a flowing stream of zeolitically dry oxygen gas (790 Torr), followed by cooling to 21 °C, and evacuating at 2×10^{-6} Torr for 20 minutes. After cooling to room temperature, each crystal, still under vacuum, was sealed in its capillary by a torch. Both crystals had become pale orange after dehydration.

The cubic space group $Fd\bar{3}$ was used throughout this work. This choice appeared to be appropriate because most crystals made from this synthesis batch have been refined successfully in $Fd\bar{3}$ with mean Al-O distances correctly longer than mean Si-O distances.

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 MoKα radiation (Kα_1, $\lambda = 0.70930$; Kα_2, $\lambda = 0.71359$ Å). The cubic unit cell constants at 21(1) °C, determined by least-squares refinement of 25 intense reflections for which $14° < 2\theta < 22°$, are $a = 24.758(4)$ Å for $Ag_{27}Tl_{65}$-X and 24.947(4) Å for $Ag_{23}Tl_{69}$-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 1351 unique reflections measured for $Ag_{27}Tl_{65}$-X and the 1386 for $Ag_{23}Tl_{69}$-X, only 375 and 235 reflections, respectively, for which $I > 3\sigma(I)$, were used in subsequent structure determination. An absorption correction (for $Ag_{27}Tl_{65}$-X, $\mu R = 1.86$, $\rho_{cal} = 3.023$ g/cm^3; for $Ag_{23}Tl_{69}$-X, $\mu R = 1.91$, $\rho_{cal} = 2.996$ g/cm^3) was made empirically using a Ψ scan for each crystal.[14] The calculated transmission coefficients ranged from 0.982 to 0.989 for $Ag_{27}Tl_{65}$-X, and from 0.985 to 0.995 for $Ag_{23}Tl_{69}$-X. This correction had little effect on the final R indices. Other details are the same as previously reported.[15]

Structure Determination

$Ag_{27}Tl_{65}$-X. 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 Ag_{92}-X.[16] Isotropic refinement converged to an unweighted R_1 index, $(\Sigma|F_o-|F_c||/\Sigma F_o)$, of 0.57 and a wR_2 index, $(\Sigma w(F_o-|F_c|)^2/\Sigma wF_o^2)^{1/2}$, of 0.67.

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 18.9 and 11.0 eÅ^{-3}, respectively. Isotropic refinement including them as Tl(2) and Ag(1), respectively, converged to $R_1 = 0.37$ and $wR_2 = 0.48$ with occupancies of 31.6(2) and 25.0(3), respectively.

It is easy to distinguish Ag^+ from Tl^- ions for several reasons. First, their atomic scattering factors are quite different (46 e$^-$ for Ag^- and 80 e$^-$ for Tl^-). Secondly, their ionic radii are different ($Ag^- = 1.26$ and $Tl^- = 1.47$ Å).[17] Also, the approach distances between those ions and oxygens in the zeolite framework in dehydrated Tl_{92}-X[7] and dehydrated Ag_{92}-X[18] have been determined and are indicative. Finally,

the requirement that the cationic charges sum to +92 per unit cell does not allow the major positions to refine to acceptable occupancies with an alternative assignment of ionic identities.

A subsequent difference Fourier function revealed two additional peaks at (0.080, 0.080, 0.80) with a height of 20.9 eÅ^{-3} and (0.184, 0.184, 0.184) with a height of 17.9 eÅ^{-3}. Inclusion of these peaks as ions at Tl(1) and Ag(2) lowered the error indices to $R_1 = 0.23$ and $wR_2 = 0.32$. The occupancy numbers at Tl(1) and Ag(2) refined to 17.4(2) and 12.0(2), respectively.

On an ensuing difference Fourier function, one peak appeared; at Tl(3), (0.416, 0.136, 0.124), height 15.1 eÅ^{-3}. A simultaneous positional and isotropic thermal parameter refinement of varying occupancy numbers varying converged to the error indices $R_1 = 0.12$ and $wR_2 = 0.14$ with an occupancy of 27.3(3).

Anisotropic thermal parameters of framework atoms were refined to negative values, which were physically unacceptable. Isotropic refinement of the framework atoms and anisotropic refinement of all Tl^+ positions and all Ag^- positions converged to $R_1 = 0.053$ and $wR_2 = 0.056$. The occupancies at Ag(1), Ag(2), Ag(3) and Ag(4) were fixed at the values shown In Table 1(a). The final error indices for the 375 reflections for which $I > 3\sigma(I)$ were $R_1= 0.055$ and $wR_2 = 0.057$.

$Ag_{23}Tl_{69}$-X. 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 $Ag_{27}Tl_{65}$-X. Isotropic refinement converged to $R_1 = 0.58$ and $wR_2 = 0.66$.

A difference Fourier function revealed two large peaks at (0.251, 0.251, 0.251) and (0.0, 0.0, 0.0) with heights of 15.3 and 5.7 eÅ^{-3}, respectively. Isotropic refinement including them as Tl(2) and Ag(1), respectively, converged to $R_1 = 0.32$ and $wR_2 = 0.45$ with occupancies of 23.2(2) and 15.2 (2), respectively.

A subsequent difference Fourier function revealed two additional peaks at (0.075, 0.075, 0.075) and (0.413, 0.134, 0.113) with heights of 19.8 and 10.4 eÅ^{-3}, respectively. Inclusion of these peaks as ions at Tl(1) and Tl(3) lowered the error indices to $R_1 = 0.10$ and $wR_2 = 0.12$. The occupancy numbers at Tl(1) and Tl(3) refined to 17.1(2) and 21.7(3), respectively.

On an ensuing difference Fourier function, two peaks appeared; at Ag(2), (0.196, 0.196, 0.196), height 4.8 eÅ^{-3}, and at Tl(4), (0.413, 0.077, 0.072), height 1.9 eÅ^{-3}. A simultaneous positional and isotropic thermal parameter refinement of varying occupancy numbers converged to the error indices $R_1 = 0.086$ and $wR_2 = 0.091$. The occupancy numbers at Ag(2) and Tl(4) refined to 7.2(5) and 4.6(4), respectively.

Anisotropic thermal parameters of framework atoms refined negative definite and physically unacceptable. Isotropic refinement of the framework atoms and anisotropic refinement of the Tl^+ positions and Ag^- positions, except Ag(2) and Tl(4) which were refined isotropically, converged to $R_1=$

Table 1. Positional, Thermal, and Occupancy Parameters[a]

(a) $Ag_{27}Tl_{65}$-X

Atom	Wyc. Pos.	Site	x	y	z	[b]U_{11} or [d]U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	[c]Occupancy varied	fixed
Si	96(g)		-508(2)	1244(3)	358(2)	143(13)							96
Al	96(g)		-518(3)	369(2)	1232(3)	110(13)							96
O(1)	96(g)		-1044(6)	-1(7)	1004(6)	289(42)							96
O(2)	96(g)		-7(7)	-14(8)	1489(6)	329(40)							96
O(3)	96(g)		-243(6)	740(6)	699(6)	217(41)							96
O(4)	96(g)		-736(6)	794(6)	1733(6)	201(36)							96
Ag(1)	16(c)	I	0	0	0	282(11)	282(11)	282(11)	46(16)	46(16)	46(16)	14.6(1)	15
Ag(2)	32(e)	II'	1839(2)	1839(2)	1839(2)	254(23)	254(23)	254(23)	2(26)	2(26)	2(26)	12.0(2)	12
Tl(1)	32(e)	I'	813(1)	813(1)	813(1)	657(14)	657(14)	657(14)	-182(14)	-182(14)	-182(14)	17.4(2)	17
Tl(2)	32(e)	II	2561(1)	2561(1)	2561(1)	277(6)	277(6)	277(6)	1(9)	1(9)	1(9)	20.2(1)	20
Tl(3)	96(g)	III'	4107(1)	1394(3)	1160(4)	199(19)	1195(64)	1932(64)	133(30)	-132(44)	-121(48)	27.3(3)	28

(b) $Ag_{23}Tl_{69}$-X

Atom	Wyc. Pos.	Site	x	y	z	[b]U_{11} or [d]U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	[c]Occupancy varied	fixed
Si	96(g)		-527(4)	1247(5)	354(4)	45(20)							96
Al	96(g)		-531(4)	359(4)	1219(5)	24(21)							96
O(1)	96(g)		-1074(9)	-36(12)	1040(9)	151(61)							96
O(2)	96(g)		-34(13)	-38(12)	1464(8)	186(53)							96
O(3)	96(g)		-286(10)	732(10)	680(9)	118(64)							96
O(4)	96(g)		-710(8)	787(9)	1768(9)	46(49)							96
Ag(1)	16(c)	I	0	0	0	444(20)	444(20)	444(20)	320(35)	320(35)	320(35)	15.2(2)	15
Ag(2)	32(e)	II'	1985(10)	1985(10)	1985(10)	1104(152)						7.2(5)	8
Tl(1)	32(e)	I'	762(2)	762(2)	762(2)	665(25)	665(25)	665(25)	-1(31)	-1(31)	-1(31)	17.1(2)	17
Tl(2)	32(e)	II	2531(1)	2531(1)	2531(1)	327(7)	327(7)	327(7)	55(19)	55(19)	55(19)	23.2(2)	24
Tl(3)	96(e)	III'	4093(3)	1357(7)	1107(5)	140(40)	1709(116)	944(112)	219(85)	-161(56)	-336(76)	21.7(3)	22
Tl(4)	96(g)	III'	4129(29)	766(32)	721(31)	1744(272)						4.6(4)	6

[a]Origin at center of symmetry. Positional and thermal parameters ($Å^2$) 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 $= \exp[(-2\pi^2 a^2)(U_{11}h_1^2+U_{22}k_2^2+U_{33}l_2^2+2U_{12}hk-2U_{13}hl+2U_{23}kl)]$. [c]Occupancy factors are given as the number of atoms or ions per unit cell. [d]$B_{iso} = 8\pi^2 U_{iso}$.

0.057 and $wR_2 = 0.056$. The occupancies of Ag(1), Ag(2), Tl(1), Tl(2) and Tl(3) were fixed at the values shown in Table 1(b). The final error indices for the 235 reflections for which $I > 3\sigma(I)$ were $R_1 = 0.058$ and $wR_2 = 0.057$.

Both crystals. The shifts in the final cycle of least-squares refinements were less than 0.1% of their corresponding standard deviations for both crystals. All crystallographic calculations were done using MolEN.[19] Atomic scattering factors[20] for Si, Al, O⁻, Ag⁺ and Tl⁻ were used. All scattering factors were modified to account for anomalous dispersion.[21,22] The quantity minimized in the least-squares treatment was $\Sigma w(F_o-|F_c|)^2$, where weights (w) are the reciprocal squares of $\sigma(F_o)$, the standard deviation of each observation. In total, 45 and 48 parameters for $Ag_{27}Tl_{65}$-X and $Ag_{23}Tl_{69}$-X, respectively, were varied; of course, the 24 parameters describing the zeolite framework differ little from those in the previous zeolite X structures, and may be omitted from the calculation of an over determination ratio: $375/21 = 17.9$ for $Ag_{27}Tl_{65}$-X and $237/24 = 9.9$ for $Ag_{23}Tl_{69}$-X. The final structural parameters are listed in Table 1 and selected interatomic distances and angles are presented in Table 2.

Discussion

Zeolite X. Zeolite X is a synthetic Al-rich analogue 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 Figure 1). These β-cages are connected tetrahedrally at six-rings by bridging oxygens to give double six-rings (D6Rs, hexagonal prisms) and, concomitantly, an interconnected set of even larger cavities (supercages) accessible in three dimensions through 12-ring (24-membered) windows. The Si and Al atoms occupy the 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

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

	Ag$_{27}$Tl$_{65}$-X	Ag$_{23}$Tl$_{69}$-X
Si-O(1)	1.59(2)	1.56(3)
Si-O(2)	1.64(2)	1.65(3)
Si-O(3)	1.64(2)	1.64(3)
Si-O(4)	1.63(2)	1.57(3)
Average	**1.63**	**1.60**
Al-O(1)	1.69(2)	1.74(3)
Al-O(2)	1.70(2)	1.70(3)
Al-O(3)	1.75(2)	1.75(3)
Al-O(4)	1.72(2)	1.79(3)
Average	**1.72**	**1.75**
Ag(1)-O(3)	2.59(2)	2.59(2)
Ag(2)-O(2)	2.51(2)	2.34(3)
Tl(1)-O(3)	2.64(2)	2.63(2)
Tl(2)-O(2)	2.660(14)	2.66(2)
Tl(3)-O(4)	2.69(2)/2.79(2)	2.78(2)/2.89(2)
Tl(4)-O(1)		2.79(8)/3.05(8)
O(1)-Si-O(2)	112.6(9)	113.5(16)
O(1)-Si-O(3)	110.9(8)	110.0(4)
O(1)-Si-O(4)	107.2(8)	105.7(13)
O(2)-Si-O(3)	105.5(9)	106.1(13)
O(2)-Si-O(4)	110.0(8)	109.0(13)
O(3)-Si-O(4)	110.7(8)	113.0(13)
O(1)-Al-O(2)	113.4(9)	109.3(15)
O(1)-Al-O(3)	109.4(8)	112.2(13)
O(1)-Al-O(4)	109.3(8)	109.9(12)
O(2)-Al-O(3)	106.7(8)	109.4(13)
O(2)-Al-O(4)	107.7(8)	104.7(12)
O(3)-Al-O(4)	110.3(8)	111.1(12)
Si-O(1)-Al	143.0(11)	135.4(15)
Si-O(2)-Al	133.3(10)	137.8(14)
Si-O(3)-Al	129.2(10)	132.3(15)
Si-O(4)-Al	140.5(10)	146.0(15)
O(3)-Ag(1)-O(3)	98.8(5)	94.9(7)
O(2)-Ag(2)-O(2)	91.0(5)	108.0(10)
O(3)-Tl(1)-O(3)	79.5(5)	83.7(7)
O(2)-Tl(2)-O(2)	84.5(6)	91.5(10)
O(4)-Tl(3)-O(4)	73.7(5)	75.3(7)
O(1)-Tl(4)-O(1)		121.0(3)

[a]Numbers in parentheses are estimated standard deviations in the units of the least significant digit given for the corresponding values.

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.[23,24]

Ag$_{27}$Tl$_{65}$-X. The mean values of the Si-O and Al-O bond lengths are 1.62 and 1.70 Å, respectively. These values are normal. The individual bond lengths, however, show marked variations: Si-O from 1.59(2) to 1.64(2) Å and Al-O from 1.69(2) to 1.75(2) Å, because the Si-O and Al-O distances depend on the coordination of Ag$^-$ and Tl$^+$ ions with the framework oxygen of O(2) and O(3) (see Table 2).

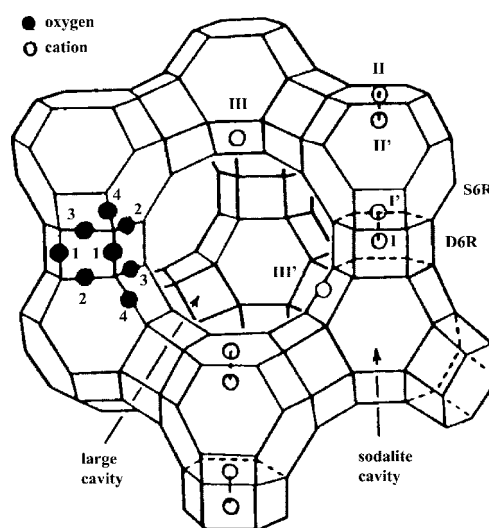In this structure, 27 Ag$^-$ ions are found at two crystallo-

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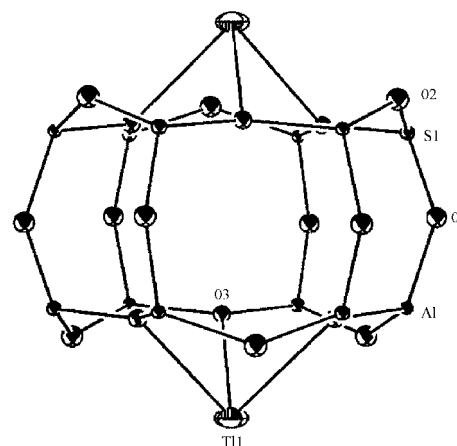

Figure 2. A double six-ring in dehydrated Ag$_{27}$Tl$_{65}$-X. Two Tl$^+$ ion at Tl(1) (site I'). About 6.25% of double six-rings may have this arrangement. Ellipsoids of 20% probability are shown.

graphic sites, and 65 Tl$^-$ ions occupy three crystallographic sites. When the mole ratio of Ag$^-$ to Tl$^-$ ions in the exchange solution was 1 : 5, only 29% of the total cations were exchanged by Ag$^-$ ions. 15 Ag$^-$ ions at Ag(1) are located at octahedral site I, at the centers of the D6Rs (see Figure 3). Each Ag$^+$ ion is coordinated by six O(3) oxygen atoms at 2.59(2) Å, approximately the sum of the conventional ionic radii of Ag$^-$ and O^{2-}, 1.26 + 1.32 = 2.58 Å.[17] so site I is able to accommodate Ag$^-$ ions nicely.

The remaining 12 Ag$^+$ ions at Ag(2) lie at site II', inside the sodalite cavities opposite the S6Rs (see Figure 3). Each Ag$^-$ ion is recessed 1.42 Å into the sodalite from the plane of the three O(2) framework oxygens to which it binds. The Ag(2)-O(2) distance is 2.51(2) Å, which is almost the same as the sum of the ionic radii, 2.58 Å.[17]

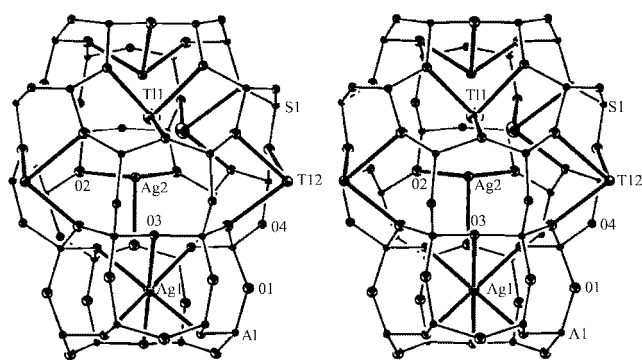Seventeen Tl$^+$ ions at Tl(1) occupy site I', in the sodalite

Figure 3. Stereoview of a sodalite cavity with an attached D6R in dehydrated Ag₂Tl₆₅-X. One Ag⁻ ion at Ag(1) (site I), two Ag⁻ ions at Ag(2) (site II'), two Tl⁺ ions at Tl(1) (site I') and two Tl⁺ ions at Tl(2) (site II) are shown. About 50% of sodalite cavities may have this arrangement. Ellipsoids of 20% probability are used.
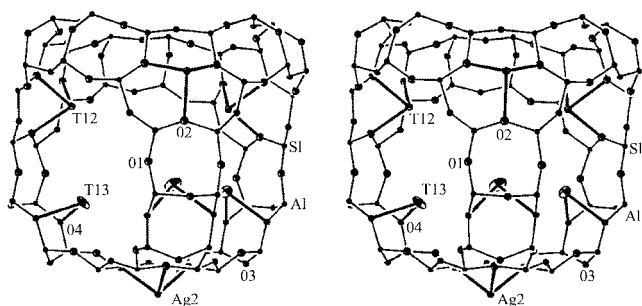

Figure 4. Stereoview of a supercage in dehydrated Ag₂-Tl₆₅-X. Two Ag⁻ ions at Ag(2) (site II'), two Tl⁻ ions at Tl(2) (site II) and three Tl⁻ ions at Tl(3) (site III') are shown. About 50% of supercages may have an arrangement like this. Ellipsoids of 20% probability are used.

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

	Ag₂-Tl₆₅-X	Ag₂₃Tl₆₉-X
At O(3)[a]		
Ag(1)	-1.71	-1.62
Tl(1)	1.78	1.67
At O(2)[b]		
Ag(2)	-1.42	-0.84
Tl(2)	1.68	1.52

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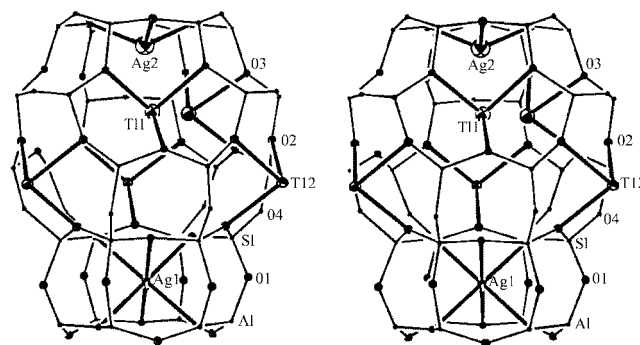

Figure 5. Stereoview of a sodalite cavity with an attached D6R in dehydrated Ag₂₃Tl₆₉-X. One Ag⁺ ion at Ag(1) (site I), one Ag⁻ ion at Ag(2) (site II'), two Tl⁻ ions at Tl(1) (site I') and three Tl⁻ ions at Tl(2) (site II) are shown. About 87.5% of sodalite cavities may have this arrangement. Ellipsoids of 20% probability are used.

cavity opposite the D6Rs (see Figures 2 and 3). The Tl(1)-O(3) distance, 2.64(2) Å, is shorter than the sum of the ionic radii of Tl⁻ and O²⁻, 1.47 + 1.32 = 2.79 Å.[17] Two Tl⁻ ions at Tl(1) have electrostatic repulsion in each of the sodalite cavities. These ions push each other to the charged oxygen planes to achieve the stabilized positions in that cavity. This makes the bond distances of Tl(1)-O(3) shorter than the sum of the corresponding ionic radii.

Twenty Tl⁺ ions at Tl(2) lie at site II and are recessed *ca.* 1.68 Å into the supercage from the S6R plane at O(2) (see Figures 3, 4, and Table 3). The Tl(2)-O(2) distance, 2.660(14) Å, is much shorter than the sum of the conventional radii of Tl⁺ and O²⁻, 2.79 Å,[17] indicative of a strong covalent interaction. The sum of the occupancy numbers at site II (Tl(2)) and site II' (Ag(2)) is 20 + 12 = 32, so that the S6Rs are fully occupied.

The remaining 28 Tl⁺ ions at Tl(3) occupy site III' positions in the supercage (see Figure 4). The Tl(3)-O(4) bond length, 2.69(2) and 2.79(2) Å, is nearly the same as the sum of the ionic radii, 2.79 Å.[17]

Ag₂₃Tl₆₉-X. In this structure, 23 Ag⁻ ions are found at two different crystallographic sites and 69 Tl⁻ ions are found at four different crystallographic sites. When the mole ratio of Ag⁺ to Tl⁻ ions in the exchange solution was 1 : 10, only

25% of the total cations were exchanged by Ag⁺ ions. Fifteen Ag⁺ ions at Ag(1) occupy the octahedral site I at the centers of the D6Rs (see Figure 5). Each Ag⁻ ion is coordinated by six O(3) oxygen atoms at 2.59(2) Å, approximately the sum of the conventional ionic radii of Ag⁻ and O²⁻, 2.58 Å.[17]

Eight Ag⁻ ions at Ag(2) lie at site II', inside the sodalite cavities opposite the S6Rs (see Figure 5). Each Ag(2) ion is recessed *ca.* 0.84 Å into the sodalite cavity from its six-ring plane (see Table 3). The distance between Ag(2) and its nearest framework oxygens at O(2) is 2.34(3) Å. This distance is much shorter than the sum of the ionic radii, 2.58 Å,[17] for reasons of covalency and low coordination number.

About 17 Tl⁺ ions at Tl(1) occupy site I', in the sodalite cavity opposite the D6Rs (see Figure 5). The Tl(1)-O(3) bond distance, 2.63(2) Å, is shorter than the sum of the ionic radii of Tl⁻ and O²⁻, 1.47 + 1.32 = 2.79 Å.[17] indicative of a strong polar covalent interaction. Twenty-four Tl⁺ ions at Tl(2) lie at site II, inside the supercage. Each Tl⁺ ion at Tl(2) coordinates at *ca.* 2.66(2) Å to three O(2) framework oxygens, and is recessed *ca.* 1.52 Å into the supercage from their plane.

Finally, 28 Tl⁻ ions occupy two different III' sites, Tl(3) and Tl(4), in the supercage, with occupancies of 22 and 6, respectively (see Figure 6). The bond distances of Tl-O (Tl(3)-O(4): 2.78(2) and 2.89(2) Å, Tl(4)-O(1): 2.79(8) and 3.05(8) Å) are similar to those found in several other dehydrated structures.[10,11,25]
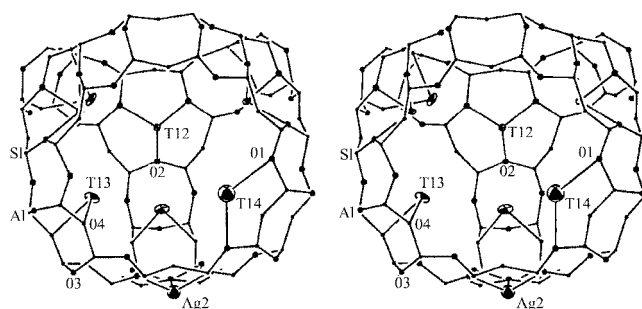
Figure 6. Stereoview of a supercage of dehydrated $Ag_{23}Tl_{69}$-X. One Ag^+ ion at $Ag(2)$ (site II'), three Tl^- ions at $Tl(2)$ (site II), three Tl^+ ions at $Tl(3)$ (site III') and one Tl^+ ion at $Tl(4)$ (site III') are shown. About 50% of supercages may have this arrangement. Ellipsoids of 20% probability are used.

Table 4. Distribution of Nonframework Atoms over Sites

	$Ag_{27}Tl_{65}$-X	$Ag_{23}Tl_{69}$-X
Sites		
I	15 Ag(1)	15 Ag(1)
I'	17 Tl(1)	17 Tl(1)
II	20 Tl(2)	24 Tl(2)
II'	12 Ag(2)	8 Ag(2)
III'	28 Tl(3)	22 Tl(3)
	–	6 Tl(4)

Conclusion

This work indicates not only that all of Na^- ions in zeolite X can be replaced readily by Ag^+ and Tl^+ ions but also that full dehydration to yield relatively simple structures is possible. The distribution of the nonframework atoms over the sites of two structures is given in Table 4. The ionic size governs the competition for site I for both structures. The small Ag^+ ions nearly fill site I, with the remainder going to site II'. The Tl^+ ion is apparently too large to occupy the center of the double 6-ring. The large Tl^+ ions, which are less able to balance the anionic charge of the zeolite framework, occupy sites I', II and III'. The bond distances of Tl-O are different, so that most of the Tl^- ions form ionic bonds with framework oxygens when they are in the supercage, whereas they show some covalent character in the sodalite cavity.

Supporting Information Available: Tables of calculated and observed structure factors (16 pages) are available from the corresponding author upon request.

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