

Two Crystal Structures of Fully Dehydrated, Fully Ag⁺-Exchanged Zeolite X. Dehydration in Oxygen Prevents Ag⁺ Reduction. Without Oxygen, Ag₈ⁿ⁺ (*T_d*) and *cyclo*-Ag₄^{m+} (near *S₄*) Form

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Two crystal structures of fully dehydrated, fully Ag⁺-exchanged zeolite X have been determined by single-crystal X-ray diffraction techniques. Ion exchange was accomplished by allowing 0.05 M aqueous AgNO₃ to flow past each crystal for 3 days to give hydrated Ag₉₂Si₁₀₀Al₉₂O₃₈₄. One crystal was dehydrated at 400 °C for 2 days, followed by cooling to 21 °C, all in a flowing stream of dry oxygen gas (790 Torr), followed by evacuation at 2 × 10⁻⁶ Torr for 20 min. The structure was determined in the cubic space group *Fd* $\bar{3}$ *m* (*a* = 25.177(4) Å) and was refined to the final error indices *R*₁ = 0.048 and *R*₂ = 0.078 with 291 reflections for which *I* > 3σ(*I*). The second crystal (*a* = 24.871(4) Å) was similarly dehydrated without oxygen. Its structure was determined in *Fd* $\bar{3}$ and refined to *R*₁ = 0.069 and *R*₂ = 0.072 with 320 reflections as above. In the first crystal, 4 Ag⁺ ions were found at the octahedral site I (Ag⁺–O = 2.689(7) Å) and 24 Ag⁺ ions occupy the nearby site I' positions (Ag⁺–O = 2.220(10) Å), avoiding I–I' contacts. Thirty-two Ag⁺ ions fill site II (Ag⁺–O = 2.360(10) Å), and the remaining 32 Ag⁺ ions occupy a III' site (Ag⁺–O = 2.368(12) and 2.586(15) Å). No reduction of Ag⁺ has occurred. In the second crystal, 16 Ag⁺ ions fill site I (Ag⁺–O = 2.573(10) Å), 32 partially reduced Ag⁺ ions half fill two different site I' positions that are unusually deep in the sodalite cavities (Ag–O = 2.628(10) and 2.708(14) Å), and 16 Ag⁺ ions half fill the 32-fold site II' inside the sodalite cavity (Ag⁺–O = 2.461(11) Å). Sixteen Ag⁺ ions half fill the 32-fold site II (Ag⁺–O = 2.231(11) Å), and eight Ag⁺ ions lie at two different III' sites. In total, only about 86 silver atoms or ions were found per unit cell of crystal 2. The remaining six have migrated out of the zeolite framework to form small silver crystallites on the surface of the zeolite single crystal. In this structure, each sodalite cavity hosts a cationic silver cluster. In half, eight silver atoms form interpenetrating tetrahedra, Ag₈ⁿ⁺, with *T_d* symmetry. The other half host *cyclo*-Ag₄^{m+} cations with near *S₄* symmetry. Likely values of *n* and *m* are 4 and 2, respectively.

Introduction

The structures of small metal clusters are of great interest, in part because of their pronounced catalytic activity. Silver ions can be reduced intrazeolitically by heating,^{1,2} by reaction with reducing agents,³ or by sorption of metal atoms.⁴ Tsutsumi and Takahashi reported that the Ag⁺ ions in zeolite Y can be reduced to bulk clusters of Ag⁰ after treatment with alcohol and alkylbenzene above 300 °C.⁵ Kim and Seff found octahedral hexasilver molecules each coordinated to eight silver ions in the sodalite units of vacuum-dehydrated, fully Ag⁺-exchanged zeolite A.² They also found a (Ag⁺)₆(Ag₆) cluster in the sodalite cavities of an ethylene sorption complex of partially decomposed, fully Ag⁺-exchanged zeolite A.⁶ In the structure of Ag_{4.6}Na_{7.4}-A vacuum-dehydrated and treated with H₂ at 350 °C, (Ag₆)³⁺ clusters of low symmetry were found in the large cavities.⁷ A review of silver chemistry and structure in zeolites is available.⁸

Beyer found that about 70% of the Ag⁺ ions in zeolite A were reducible by hydrogen after dehydration at 150 °C and that about 92% of the Ag⁺ ions were reducible after dehydration at 330 °C.⁹ Beyer, Jacobs, and Uytterhoeven reported that polynuclear cations of mean or approximate composition Ag₃⁺ form upon partial reduction of dehydrated, fully Ag⁺-exchanged zeolite Y.¹⁰

The redox reactions of Ag–Y with oxygen and hydrogen were studied using powder X-ray diffraction techniques.¹¹ When Ag–Y was dehydrated, Ag₃²⁺ clusters were seen to have formed by “autoreduction”, reaction of Ag⁺ ions with zeolite oxygen atoms to release oxygen gas: 4Ag⁺ + 2O²⁻ → 4Ag⁰ + O₂, followed by 2Ag⁺ + Ag⁰ → Ag₃²⁺.¹² When this zeolite was treated with oxygen at 600 °C, the Ag⁰ atoms and Ag⁺ ions in these partially reduced clusters were seen to migrate from general (reduced) silver positions in the supercages to cation positions in the sodalite units and in the D6Rs.¹² Lee et al.¹³ studied the crystal structure of Ag₉₂–X fully dehydrated at 360 °C in flowing oxygen followed by the removal of O₂(g) by evacuation at 400 °C before subsequent cooling. This evacuation

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of O₂(g) at 400 °C appears to have led to the formation of eight Ag atoms per unit cell by "autoreduction", resulting in the formation of three Ag₃⁺ and two Ag₃²⁺ clusters.

This work was done to see whether fully dehydrated, fully Ag⁺-exchanged zeolite X could be prepared without any reduction of Ag⁺ by keeping the crystal in an oxygen atmosphere, both at elevated temperature (during dehydration) and during subsequent cooling to ambient temperature. This composition was sought because it would be ideal (except for Si/Al ≠ 1 in the zeolite framework) for the study of the sorption complexes and chemistry of Ag⁺ in zeolite X. Ag⁺ ions in zeolite X are reduced upon dehydration in the absence of oxygen.^{11,14} For comparison, this work was repeated for a second crystal dehydrated identically in the absence of oxygen.

Experimental Section

Large single crystals of zeolite Na-X, stoichiometry Na₉₂Si₁₀₀Al₉₂O₃₈₄, were prepared in St. Petersburg, Russia.¹⁵ Two of these, colorless octahedra about 0.2 mm in cross section, were lodged in two fine Pyrex capillaries.

An aqueous exchange solution of 0.05 M AgNO₃ was allowed to flow past each crystal for 3 days. The capillary containing the first crystal was attached to a vacuum system, and the crystal was dehydrated at 400 °C for 2 days, followed by cooling to 21 °C, all in a flowing stream of zeolitically dry oxygen gas (790 Torr), followed by evacuation at 2 × 10⁻⁶ Torr for 20 min. That crystal, still under vacuum, still colorless, was then sealed in its capillary by torch. The second crystal was similarly dehydrated under vacuum (without oxygen). After cooling to room temperature and while still under vacuum, the now dark gray crystal was sealed in its capillary by torch.

The reflection conditions (*hkl*—*h* + *k*, *k* + *l*, *l* + *h* = 2*n*; 0*kl*—*k* + *l* = 4*n*) indicate that the space group is either *Fd* $\bar{3}$ or *Fd* $\bar{3}m$. *Fd* $\bar{3}$ was initially chosen for the first crystal because most crystals from this synthesis batch, regardless of subsequent chemical treatment, refined successfully in *Fd* $\bar{3}$.¹⁶ However, *Fd* $\bar{3}$ was rejected, and the space group *Fd* $\bar{3}m$ was chosen because an insignificant difference (0.001 Å) was seen in least-squares refinement between the mean Al—O and Si—O distances. In addition, the error indices did not increase when the space group was changed to *Fd* $\bar{3}m$. The near equality of the Al—O and Si—O distances indicates that the Si/Al composition at the Si position is essentially the same as that for the entire crystal; the same is necessarily true at the Al position. It is unclear why the long-range Si,Al ordering is absent. It may have been absent initially in the crystal selected, or it may have been lost in chemical treatment.^{16,17}

For the second crystal, the cubic space group *Fd* $\bar{3}$ was used. This choice is supported by (a) the low Si/Al ratio, which requires, at least in the short range, alternation of Si and Al, and (b) the observation that this crystal, like at least most other crystals from the same batch,¹⁵ does not have intensity symmetry across (110) and therefore lacks that mirror plane. Unlike crystal 1, this choice is supported by the final results: the Al—O bonds are all longer than the Si—O bonds.

Diffraction data were collected with an automated Enraf-Nonius four-circle computer-controlled CAD-4 diffractometer equipped with a pulse-height analyzer and a graphite monochromator, using Mo K α radiation (K α ₁, λ = 0.709 30; K α ₂, λ = 0.713 59 Å). The cubic unit cell constants at 21(1) °C, determined by least-squares refinement of 25 intense reflections for which 14° < 2 θ < 22°, are *a* = 25.177(4) Å for crystal 1 and 24.871(4) Å for crystal 2. All unique reflections in the positive octant of an *F*-centered unit cell for which 2 θ < 50°,

l > *h*, and *k* > *h* were recorded. Of the 1418 unique reflections measured for crystal 1 and 1368 for crystal 2, only the 291 and 320 reflections, respectively, for which *I* > 3 σ (*I*) were used in subsequent structure determination. An absorption correction (for crystal 1, μR = 0.47, ρ_{cal} = 2.222 g/cm³; for crystal 2, μR = 0.47, ρ_{cal} = 2.259 g/cm³) was made empirically using a ψ scan for each crystal.¹⁸ The calculated transmission coefficients ranged from 0.985 to 0.992 for crystal 1 and from 0.982 to 0.987 for crystal 2. This correction had little effect on the final *R* indices. Other details are the same as previously reported.¹⁹

Structure Determination

Ag₉₂-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 Cd₆₈-X.²⁰ Isotropic refinement converged to an unweighted *R*₁ index, ($\sum |F_o - |F_c|| / (\sum F_o)$), of 0.45 and a weighted *R*₂ index, ($\sum w(F_o - |F_c|)^2 / (\sum wF_o^2)$)^{1/2}, of 0.56.

A difference Fourier function revealed two large electron-density peaks at (0.032, 0.032, 0.032) and (0.221, 0.221, 0.221) with heights of 24 and 17 e Å⁻³, respectively. Isotropic refinement including those peaks as Ag(2) and Ag(3), respectively, converged to *R*₁ = 0.20 and *R*₂ = 0.27 with occupancies of 31.6(2) and 25.0(3), respectively. Ag(2) and Ag(3) are both 32-fold positions.

A subsequent difference Fourier function revealed two additional peaks at (0.0, 0.0, 0.0) with height 11.5 e Å⁻³ and (0.413, 0.236, 0.173) with height 3.8 e Å⁻³. Inclusion of these peaks as ions at Ag(1) and Ag(4) lowered the error indices to *R*₁ = 0.15 and *R*₂ = 0.19. The occupancy numbers at Ag(1) and Ag(4) refined to 4.7(2) and 33.1(7), respectively. These are 16-fold and 96-fold positions, respectively.

Anisotropic refinement of all framework atoms and silver positions converged to *R*₁ = 0.049 and *R*₂ = 0.070. The occupancies at Ag(1), Ag(2), Ag(3), and Ag(4) were fixed at the values shown in Table 1 (section a) considering that (no. at 1) + (no. at 1')/2 ≤ 16. The final error indices for the 291 reflections for which *I* > 3 σ (*I*) were *R*₁ = 0.048 and *R*₂ = 0.078. The final refinement was done using the 508 reflections for which *I* > 0 to make better use of the diffraction data; *R*₁ = 0.099 and *R*₂ = 0.070. This allowed the estimated standard deviations (esds) to decrease to about 30% of their former values.

Ag₈₆-X (Crystal 2). 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 Ag₉₂-X.¹³ Isotropic refinement converged to *R*₁ = 0.52 and *R*₂ = 0.61.

A difference Fourier function revealed two large peaks at (0.0, 0.0, 0.0) and (0.248, 0.248, 0.248) with heights of 19 and 11 e Å⁻³, respectively. Isotropic refinement including them as Ag(1) and Ag(4), respectively, converged to *R*₁ = 0.35 and *R*₂ = 0.46 with occupancies of 15.3(2) and 17.4(3), respectively. They are 16-fold and 32-fold positions, respectively.

A subsequent difference Fourier function revealed two additional peaks at (0.081, 0.081, 0.081) and (0.186, 0.186, 0.186) with heights of 16 and 11 e Å⁻³, respectively. Inclusion of these peaks as ions at Ag(2a) and Ag(3) lowered the error indices to *R*₁ = 0.11 and *R*₂ = 0.13. The occupancy numbers at Ag(2a) and Ag(3) refined to 30.3(3) and 16.4(3), respectively. These are both 32-fold positions.

On an ensuing difference Fourier function, two peaks appeared: at Ag(5), (0.114, 0.127, 0.395), height 2.4 e Å⁻³, and Ag(6), (0.182, 0.236, 0.400), height 0.95 e Å⁻³. Simulta-

TABLE 1: Positional, Thermal, and Occupancy Parameters^a(a) Crystal 1 (Ag₉₂-X, Dehydrated in Flowing O₂)

atom	wyc. pos.	site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁ ^b	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃	occupancy ^c	
												varied	fixed
Si,Al	192(g)		-551(1)	1249(2)	358(1)	136(15)	142(14)	94(15)	-14(23)	-2(14)	-37(19)		192
O(1)	96(h)		-1086(3)	1086(3)	0	142(41)	142(41)	177(65)	-10(46)	-43(39)	-43(39)		96
O(2)	96(g)		-35(3)	-35(3)	1395(4)	219(38)	219(38)	259(79)	-58(66)	-49(43)	-49(43)		96
O(3)	96(g)		-708(3)	-708(3)	371(4)	271(46)	271(46)	154(73)	84(64)	70(46)	70(46)		96
O(4)	96(g)		1760(3)	1760(3)	3201(5)	101(36)	101(36)	233(66)	56(57)	9(40)	9(40)		96
Ag(1)	16(c)	I	0	0	0	349(44)	349(44)	349(44)	-9(54)	-9(54)	-9(54)	4.7(2)	4
Ag(2)	32(e)	I'	364(1)	364(1)	364(1)	615(11)	615(11)	615(11)	485(14)	485(14)	485(14)	25.0(3)	24
Ag(3)	32(e)	II	2221(1)	2221(1)	2221(1)	420(7)	420(7)	420(7)	278(10)	278(10)	278(10)	31.6(2)	32
Ag(4)	96(g)	III'	4105(4)	2243(5)	1827(5)	550(61)	2066(151)	1032(82)	193(66)	-422(53)	-231(74)	33.1(7)	32

(b) Crystal 1 (Ag₈₆-X, Dehydrated in Vacuum)

atom	wyc. pos.	site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁ ^{b,d}	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃	occupancy ^c	
												varied	fixed
Si	96(g)		-509(2)	1247(2)	364(2)	223(24)	155(22)	151(23)	-90(28)	-16(22)	13(25)		96
Al	96(g)		-522(2)	372(2)	1238(2)	288(27)	113(24)	148(23)	31(24)	-68(31)	47(27)		96
O(1)	96(g)		-1037(4)	2(4)	996(4)	233(64)	558(74)	360(67)	-263(62)	-166(54)	-264(63)		96
O(2)	96(g)		11(5)	-13(5)	1468(4)	371(67)	488(71)	386(68)	221(65)	-20(67)	-43(70)		96
O(3)	96(g)		-264(4)	720(4)	694(4)	456(71)	302(70)	274(67)	103(67)	235(64)	48(65)		96
O(4)	96(g)		-714(4)	792(4)	1731(4)	273(60)	222(58)	99(54)	-24(62)	83(60)	-30(51)		96
Ag(1)	16(c)	I	0	0	0	304(9)	304(9)	304(9)	18(11)	18(11)	18(11)	15.3(2)	16
Ag(2a)	32(e)	I'	792(1)	792(1)	792(1)	479(14)						16.5(3)	16
Ag(2b)	96(g)	I'	774(4)	745(4)	1025(3)	572(32)						15.8(3)	16
Ag(3)	32(e)	II'	1859(1)	1859(1)	1859(1)	470(15)	470(15)	470(15)	251(18)	251(18)	251(18)	17.4(3)	16
Ag(4)	32(e)	II	2333(2)	2333(2)	2333(2)	547(16)	547(16)	547(16)	358(18)	358(18)	358(18)	16.4(3)	16
Ag(5)	96(g)	III'	1077(12)	1372(13)	3989(12)	588(112)						4.6(2)	
Ag(6)	96(g)	III'	1785(28)	2540(28)	4007(27)	86(172)						1.5(2)	

^a Origin at center of symmetry. Positional and thermal parameters (Å²) 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 = $\exp[-2\pi^2/a^2(U_{11}h^2 + U_{22}k^2 + U_{33}l^2 + 2U_{12}hk + 2U_{13}hl + 2U_{23}kl)]$. ^c Occupancy factors are given as the number of atoms or ions per unit cell. ^d $B_{\text{iso}} = 8\pi^2 U_{\text{iso}}$.

neous positional and isotropic thermal parameter refinement with occupancy numbers varying converged to the error indices $R_1 = 0.10$ and $R_2 = 0.10$. The Ag(5) and Ag(6) positions, both 96-fold, are sparsely occupied (see Table 1, section b).

Anisotropic refinement of the framework atoms, except O(2), and the Ag positions, except Ag(5) and Ag(6), which were refined isotropically, converged to $R_1 = 0.068$ and $R_2 = 0.070$. The occupancies of Ag(1), Ag(2a), Ag(3), Ag(4), Ag(5), and Ag(6) were fixed at the values shown in Table 1 (section b). The final error indices for the 320 reflections for which $I > 3\sigma(I)$ were $R_1 = 0.069$ and $R_2 = 0.072$. The thermal ellipsoid at Ag(2a), however, was anomalously large ($U_{ii} = 0.10$ Å²). In subsequent refinements, Ag(2a) was refined with position and occupancy parameters varying and U_{iso} fixed at 0.05 Å². A subsequent difference Fourier synthesis showed a large peak at Ag(2b) (0.071, 0.069, 0.110). Full-matrix least-squares refinement including this peak at Ag(2b) converged to $R_1 = 0.060$ and $R_2 = 0.062$. The final refinement was done using the 722 reflections for which $I > 0$ to make better use of the diffraction data; $R_1 = 0.175$ and $R_2 = 0.061$. This allowed the esds to decrease to about 30% of their former values, as was seen with crystal 1.

Both Crystals. The shifts in the final cycles of least-squares refinement were all less than 0.1% of their corresponding standard deviations for both crystals. All crystallographic calculations were done using MolEN.²¹ Atomic scattering factors²² for (Si,Al)^{1.75+}, O⁻, and Ag⁺ were used. The function describing (Si,Al)^{1.75+} is the mean of the Si⁰, Si⁴⁺, Al⁰, and Al³⁺ functions. All scattering factors were modified to account for anomalous dispersion.^{23,24} 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 vertexes 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 (an n -ring contains n oxygens and n T (Si or Al) atoms). The Si and Al atoms occupy the vertexes 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, site I' in the sodalite cavity on the opposite side of one of the D6R's six-rings from site I, site II' inside the sodalite cavity near a single six-ring (S6R) entrance to the supercage, site II in the supercage adjacent to a S6R, site III in the supercage on a 2-fold axis opposite a four-ring between two 12-rings, and site III' off the 2-fold axis but still on the inner surface of the supercage.^{24,25}

Ag₉₂-X (Crystal 1). Ninety-two Ag⁺ ions are found at four crystallographic sites. As hoped for, there are no Ag⁰ atoms in this structure; no Ag⁺ ions were reduced during crystal preparation. This is consistent with the colorlessness of the crystal.

Four Ag⁺ ions at Ag(1) are located at octahedral site I at the centers of the D6Rs (see Figure 2). The Ag(1)-O(3) distance,

TABLE 2: Selected Interatomic Distances (Å) and Angles (deg)^a

(a) Crystal 1 (Ag ₉₂ -X, Dehydrated in Flowing O ₂)			
distance		angle	
(Si,Al)-O(1)	1.672(4)	O(1)-(Si,Al)-O(2)	111.2(3)
(Si,Al)-O(2)	1.674(6)	O(1)-(Si,Al)-O(3)	107.4(4)
(Si,Al)-O(3)	1.685(5)	O(1)-(Si,Al)-O(4)	108.8(4)
(Si,Al)-O(4)	1.650(7)	O(2)-(Si,Al)-O(3)	106.1(5)
mean	1.671	O(2)-(Si,Al)-O(4)	110.5(5)
Ag(1)-O(3)	2.689(7)	O(3)-(Si,Al)-O(4)	112.8(3)
Ag(2)-O(3)	2.220(10)	(Si,Al)-O(1)-(Si,Al)	133.4(4)
Ag(3)-O(2)	2.360(10)	(Si,Al)-O(2)-(Si,Al)	150.4(7)
Ag(4)-O(1)	2.368(12)	(Si,Al)-O(3)-(Si,Al)	140.7(6)
Ag(4)-O(4)	2.586(15)	(Si,Al)-O(4)-(Si,Al)	148.9(7)
Ag(2)···Ag(2)	3.157(4)	O(3)-Ag(1)-O(3)	91.2(3)
		O(3)-Ag(2)-O(3)	119.9(2)
		O(2)-Ag(3)-O(2)	118.5(2)
		O(1)-Ag(4)-O(4)	65.9(3)
(b) Crystal 2 (Ag ₈₆ -X, Dehydrated in Vacuum)			
distance		angle	
Si-O(1)	1.601(11)	O(1)-Si-O(2)	112.4(6)
Si-O(2)	1.610(12)	O(1)-Si-O(3)	107.6(7)
Si-O(3)	1.663(11)	O(1)-Si-O(4)	110.4(6)
Si-O(4)	1.610(10)	O(2)-Si-O(3)	104.9(6)
mean	1.621	O(2)-Si-O(4)	109.9(6)
Al-O(1)	1.689(11)	O(3)-Si-O(4)	111.6(5)
Al-O(2)	1.733(12)	O(1)-Al-O(2)	113.3(6)
Al-O(3)	1.729(11)	O(1)-Al-O(3)	106.1(6)
Al-O(4)	1.680(11)	O(1)-Al-O(4)	112.5(5)
mean	1.708	O(2)-Al-O(3)	104.5(5)
Ag(1)-O(3)	2.573(10)	O(2)-Al-O(4)	108.7(6)
Ag(2a)-O(3)	2.642(10)	O(3)-Al-O(4)	111.5(5)
Ag(2b)-O(3)	2.628(14)/2.708(14)	Si-O(1)-Al	145.7(7)
Ag(3)-O(2)	2.461(11)	Si-O(2)-Al	136.7(7)
Ag(4)-O(2)	2.231(11)	Si-O(3)-Al	130.1(7)
Ag(5)-O(4)	2.54(3)/2.64(3)	Si-O(4)-Al	144.0(7)
Ag(6)-O(1)	2.25(7)		
Ag(6)-O(4)	2.82(7)	O(3)-Ag(1)-O(3)	96.8(3)
Ag(2a)-Ag(2a)	3.22(3)	O(3)-Ag(2a)-O(3)	80.6(3)
Ag(2a)-Ag(3)	2.705(6)	O(3)-Ag(2b)-O(3)	70.8(3)
Ag(2b)-Ag(2b)	2.622(14)/2.749(13)	O(2)-Ag(3)-O(2)	95.2(4)
Ag(1)-Ag(2a)	3.411(2)	O(2)-Ag(4)-O(2)	109.1(4)
Ag(1)-Ag(2b)	3.692(9)	O(4)-Ag(5)-O(4)	79.2(9)
		O(1)-Ag(6)-O(4)	61.4(17)
		Ag(2a)-Ag(3)-Ag(2a)	73.14(9)
		Ag(3)-Ag(2a)-Ag(3)	104.59(3)
		Ag(2b)-Ag(2b)-Ag(2b)	80.0(4)

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

2.689(7) Å, is a little longer than the sum of the conventional ionic radii of Ag⁺ and O²⁻, 1.26 + 1.32 = 2.58 Å,²⁶ so site I is able to accommodate Ag⁺ ions nicely.

The 24 Ag⁺ ions at Ag(2) lie at site I', on 3-fold axes essentially in the planes of the six-rings of the D6Rs but displaced slightly into the sodalite cavity (see Figure 3 and Table 3). Each is too close to site I (because of electrostatic repulsion) for simultaneous occupancy of sites I and I' in a single D6R, so if a site I is occupied, the two adjacent I' sites cannot be. Of the 24 sites I' that are not adjacent to occupied I sites, all are occupied by Ag⁺ ions at Ag(2). The Ag(2)-O(3) distance, 2.220(10) Å, is much shorter than the sum of the ionic radii, 2.58 Å,²⁶ indicating that each Ag⁺ ion coordinates strongly with polar covalent bonds to its three O(3) oxygens, as might be expected because of this low coordination number.

The Ag(2)-Ag(2) distance is 3.157(4) Å, noticeably less than the 3.224(3)-Å Ag⁺-Ag⁺ distance found in a similar structure in which some reduction of Ag⁺ had occurred.¹³ It is just a little longer than the distances ranging from 2.655(2) to 3.058(1)

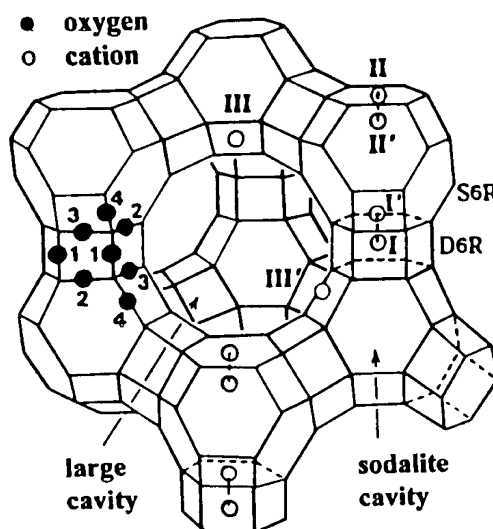


Figure 1. A stylized drawing of the framework structure of zeolite X. Near the center of each line segment is an oxygen atom. The different oxygen atoms are indicated by the numbers 1–4. Silicon and aluminum atoms alternate at the tetrahedral intersections, except that Si substitutes for about 4% of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

Å that have been reported for Ag⁺-Ag⁺ interactions in seven organic complexes of AgNO₃.^{27–33} This indicates that a weak Ag⁺-Ag⁺ interaction occurs in 12 of the 16 D6Rs per unit cell of this crystal. The Ag⁺ ions at Ag(2) do not extend away from their D6Rs to avoid a Ag⁺-Ag⁺ repulsion (see Figure 3). Such Ag⁺-Ag⁺ interactions have been eloquently discussed by Jansen.³⁴

Thirty-two Ag⁺ ions at Ag(3) fill site II, on 3-fold axes in the supercages (see Figures 3 and 4). Each Ag⁺ ion extends 0.28 Å into the supercage from the plane of the three O(2) framework oxygens to which it binds. The Ag(3)-O(2) bond length, 2.360(10) Å, is also much shorter than the sum of the ionic radii, 2.58 Å,²⁶ for reasons of covalency and low coordination number as was seen with Ag(2).

The remaining 24 Ag⁺ ions at Ag(4) occupy a III' position in the supercage (see Figure 4). The Ag(4)-O(1) bond length, 2.368(12) Å, is again shorter than the sum of the ionic radii, 2.58 Å,²⁶ indicating again that these bonds have substantial covalent character. The Ag(4)-O(4) bond length, 2.586(15) Å, is equal to this sum. The coordination number at Ag(4) is only two.

In fully dehydrated Ag₉₂-X, 92 Ag⁺ cations are found at sites I, I', II, and III'. Dehydration of Ag₉₂-X under flowing O₂ gas at 400 °C, followed by evacuation of O₂ only after the crystal had cooled to room temperature, has successfully produced (Ag⁺)₉₂-X.

It may reasonably be anticipated that sites I', II, and III would each hold 32 Ag⁺ ions in the idealized composition Ag₉₆Si₉₆-Al₉₆O₃₈₄, fully Ag⁺-exchanged zeolite LSX fully dehydrated under oxidizing conditions, for example, in flowing oxygen gas.

Ag₈₆-X (Crystal 2). In this structure, Ag atoms or ions are found at six different crystallographic sites. With four of these being half-filled 32-fold positions and with difficulty in identifying integral oxidation states for the silver atoms or ions, this structure is more complex than that of crystal 1 and much more difficult to interpret.

Sixteen Ag⁺ ions at Ag(1) fill 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 2.573(10) Å, approximately the sum of the conventional ionic radii of Ag⁺ and O²⁻, 2.58 Å.²⁶

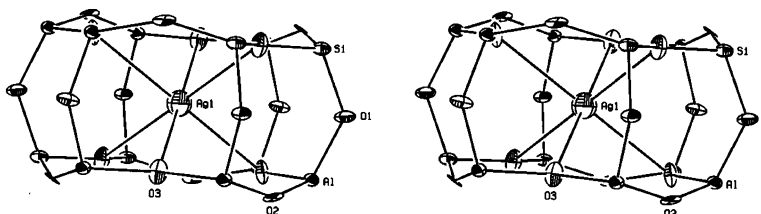


Figure 2. Stereoview of a double six-ring in $\text{Ag}_{92}\text{-X}$ dehydrated in flowing $\text{O}_2(\text{g})$. Four of the 16 D6Rs per unit cell contain a Ag^+ ion at Ag(1) (site I). Ellipsoids of 50% probability are shown.

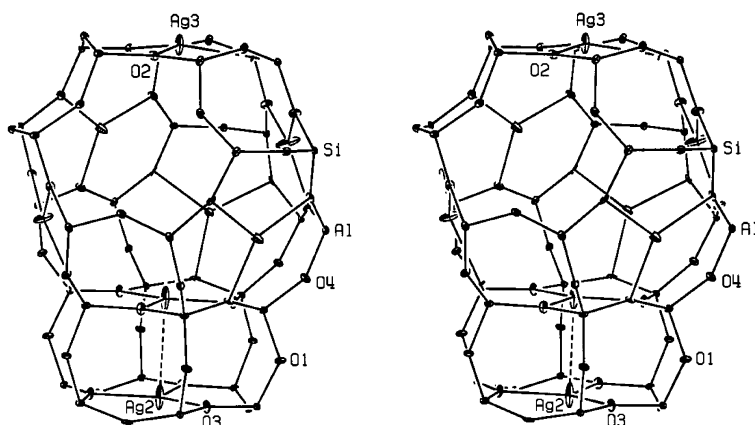


Figure 3. Stereoview of a sodalite cavity with an attached D6R in $\text{Ag}_{92}\text{-X}$ dehydrated in flowing $\text{O}_2(\text{g})$. Three Ag^+ ions at Ag(2) (site I') and four Ag^+ ions at Ag(3) (site II) are shown. All sodalite cavities may have this arrangement. Ellipsoids of 20% probability are used.

TABLE 3: Deviations (\AA) of Atoms from Six-Ring Oxygen Planes

	crystal 1	crystal 2
	At O(3) ^a	
Ag(1)	-1.52	-1.65
Ag(2)	0.07	
Ag(2a)		1.76
Ag(2b)		2.00
	At O(2) ^b	
Ag(3)	0.28	-1.28
Ag(4)		0.76

^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 negative deviation indicates that the atom lies in the sodalite cavity. A positive deviation indicates that the atom lies in the supercage.

Sixteen Ag atoms or ions at Ag(2a) and another 16 at Ag(2b) fill the 32-fold site I', in the sodalite cavity opposite the D6Rs (see Figures 5 and 6). Each atom or ion at Ag(2a) and Ag(2b) is recessed 1.76 and 2.00 \AA , respectively, into the sodalite cavity from its six-ring plane (Table 3). The distances between Ag(2a) and its three nearest framework oxygens at O(3) are 2.642(10) \AA ; for Ag(2b), the shortest distance is about the same, 2.628(14) \AA . These distances are less than the Ag^0 atom to framework oxygen distance, 2.78 \AA , in previous studies^{1,2} yet more than the sum of the ionic radii of Ag^+ and O^{2-} , 2.58,²⁶ and more than the Ag–O distances commonly seen for three-coordinate Ag^+ (see Ag(2)–O(3) and Ag(3)–O(2) in crystal 1; also see next paragraph). Accordingly, the Ag species at Ag(2a) and Ag(2b) are not easily identified as Ag^0 or Ag^+ . This will limit the conclusions that can eventually be drawn.

About sixteen Ag^+ ions at Ag(3) lie at site II' inside the sodalite cavities opposite S6Rs. This 32-fold position is also only half-occupied. The number of Ag^+ ions at Ag(4) (vide infra) appears to be equal to the number at Ag(3), so the S6Rs appear to be full. Each Ag^+ ion at Ag(3) coordinates at 2.461(11) \AA to three O(2) framework oxygens and is recessed 1.28 \AA into the sodalite cavity from their plane (Table 3).

Ag(2a)–Ag(2b) interactions cannot occur; the Ag(2a)–Ag(2b) distance is only 0.6 \AA and can be readily avoided. Ag(2a) and Ag(2b) must therefore be segregated into different sodalite cavities. The remaining question is, in the sodalite units, do the 16 Ag(3) ions bond to the 16 atoms or ions at Ag(2a) or to the 16 at Ag(2b)? The distances between Ag(2b) and Ag(3) are 2.116(7), 2.873(11), and 2.946(10) \AA . The distances between Ag(2a) and Ag(3) are all 2.705(6) \AA . The 2.116(7)- \AA Ag(2b)–Ag(3) distance is far too short to be an intersilver bond, so Ag(3) and Ag(2b) cannot occupy a sodalite unit simultaneously. Therefore, the Ag^+ ions at Ag(3) bond only with Ag atoms or ions at Ag(2a).

The distance between Ag(2a) and Ag(3) is 2.705(6) \AA , substantially shorter than the $\text{Ag}^0\text{--Ag}^0$ distance in silver metal, 2.89 \AA .³⁵ It is the same as the sum of the ionic radius of Ag^+ and the atomic radius of Ag metal, $1.26 + 1.445 = 2.705$ \AA .⁸ Therefore, this interaction may be an $\text{Ag}^0\text{--Ag}^+$ interaction. The Ag(2a)–O(3) distance, 2.642(10) \AA , is longer than Ag(3)–O(2), 2.461(11) \AA , suggesting that Ag(2a) is more reduced than Ag(3), which is more like Ag^+ . The possible arrangement of four Ag(2a) and four Ag(3) (a cube distorted to two interpenetrating tetrahedra) is shown in Figure 5. These Ag_8^{n+} clusters ($n < 8$) occupy half of the sodalite cavities and are stabilized by charge delocalization from Ag atoms to Ag^+ ions (Ag(2a) to Ag(3)). The interaction between framework oxygens and Ag species, predominantly between O(2) and Ag(3), must also contribute to the stabilization of these clusters.

In the other half of the sodalite cavities, four Ag(2b) atoms or ions form novel bent *cyclo*- Ag_4 clusters (see Figures 6 and 7). The Ag(2b)–Ag(2b) distances are 2.622(14) and 2.749(13) \AA . The mean of these two distances, 2.685 \AA , is nearly the same as that seen in Ag_8^{n+} , 2.705 \AA (vide supra). Again these appear to be too short for $\text{Ag}^0\text{--Ag}^0$ interactions but may indicate $\text{Ag}^0\text{--Ag}^+$ interactions (sum of the radii = 2.705 \AA).⁸ This *cyclo*- Ag_4^{m+} ($m < 4$) cluster nearly has S_4 symmetry. All angles are 80.0(4) $^\circ$ (Table 2, section b).

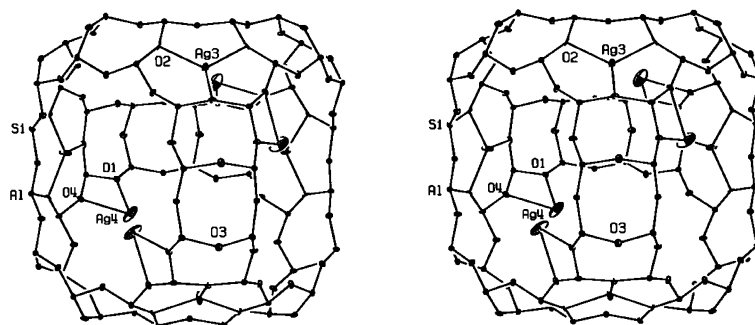


Figure 4. Stereoview of a supercage in $\text{Ag}_{92}\text{-X}$ dehydrated in flowing $\text{O}_2(\text{g})$. Four Ag^+ ions at Ag(3) (site II) and four Ag^+ ions at Ag(4) (site III') are shown. All supercages may have an arrangement like this. Ellipsoids of 20% probability are used.

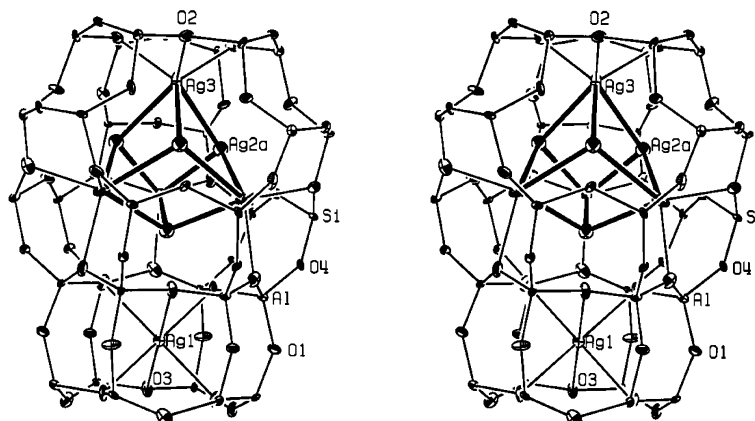


Figure 5. Stereoview of a sodalite cavity with an attached D6R in dehydrated $\text{Ag}_{86}\text{-X}$. One Ag^+ ion is shown at Ag(1) (site I). Four Ag species at Ag(2a) (site I') and four Ag^+ ions at Ag(3) (site II') form a T_d (distorted cubic) Ag_8^{n+} cluster; $n = 4$ seems most likely. Half of the sodalite cavities contain a Ag_8^{n+} cluster. Ellipsoids of 20% probability are used.

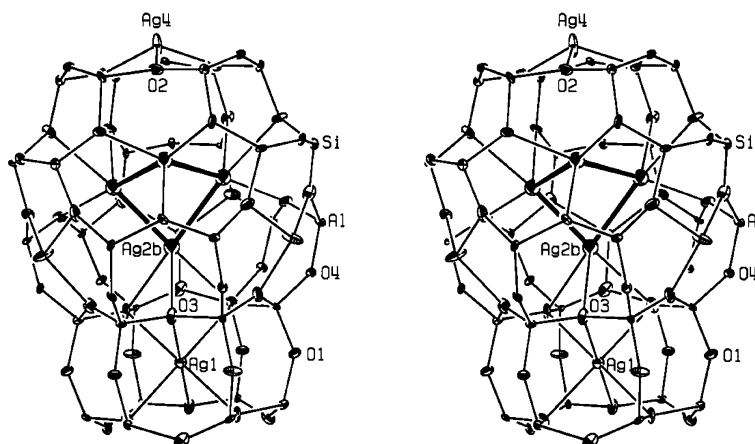
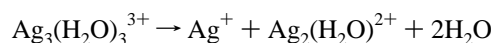


Figure 6. Stereoview of a sodalite cavity with an attached D6R in dehydrated $\text{Ag}_{86}\text{-X}$. One Ag^+ ion at Ag(1) (site I), four Ag species at Ag(2b) (site I'), and four Ag^+ ions at Ag(4) (site II) are shown. The four at Ag(2b) form *cyclo*- Ag_4^{m+} clusters; $m = 2$ seems most likely. Half of the sodalite cavities contain a Ag_4^{m+} cluster. Ellipsoids of 20% probability are used.

In a crystallographic study of zeolite A, Ag^+ ions were found to be reduced by the following reactions that occurred within the sodalite units.² The penultimate step of the dehydration process is



followed by



A similar process could be occurring in zeolite X. Alternatively, the “autoreduction” discussed in the Introduction section,

corresponding to the thermal decomposition of the Ag_2O component of the zeolite composition to the elements, could be occurring. By mass action, oxygen gas has prevented either or both processes from occurring in crystal 1.

Sixteen Ag^+ ions at Ag(4) lie at site II and extend 0.76 Å into the supercage from the S6R plane at O(2) (see Figure 8). This 32-fold position is again half-occupied. The Ag(3)–O(2) distance, 2.461(11) Å, is much shorter than the sum of the conventional radii of Ag^+ and O^{2-} , 2.58 Å, again indicative of a polar covalent interaction. The Ag^+ ions at Ag(4) do not associate with Ag species at Ag(2b): the Ag(2b)–Ag(4) distance, 3.864 Å, is too long for bonding.

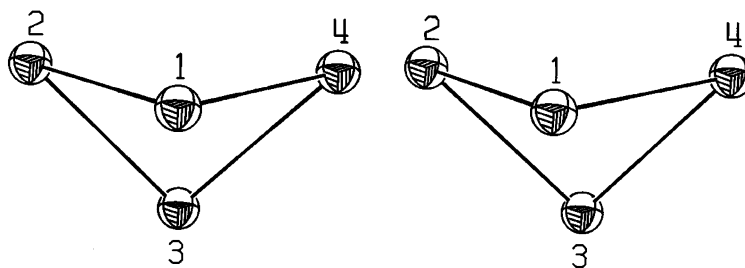


Figure 7. Stereoview of Ag_4^{n+} ; $n = 2$ seems most likely. The atoms, all $\text{Ag}(2b)$, are numbered. The 1–2 and 3–4 distances are 2.749(13) Å. The 2–3 and 4–1 distances are 2.622(14) Å. All angles are 80.0(4)°. Ellipsoids of 20% probability are used.

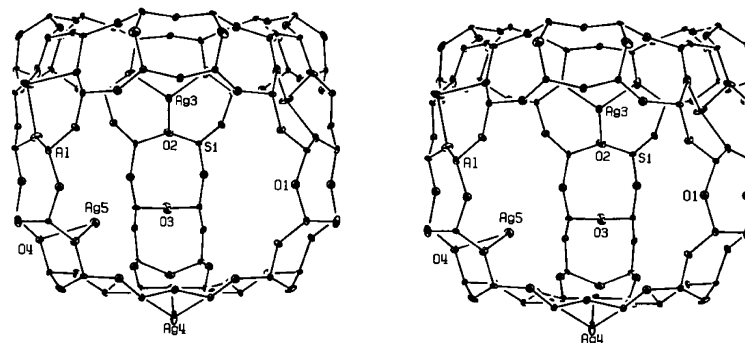


Figure 8. Stereoview of a supercage of dehydrated $\text{Ag}_{86}\text{-X}$. Two Ag^+ ions at $\text{Ag}(3)$ (site II'), two Ag^+ ions at $\text{Ag}(4)$ (site II), and one Ag^+ ion at $\text{Ag}(5)$ (site III') are shown. About 75% of supercages may have this arrangement. Ellipsoids of 20% probability are used.

The $\text{Ag}(3)\text{--Ag}(4)$ distance is 2.044(3) Å, too short to be either $\text{Ag}^+\text{--Ag}^+$ or $\text{Ag}^+\text{--Ag}^0$ interactions.¹³ Therefore, these ions should not occupy a six-ring simultaneously. The sum of the occupancy numbers at site II ($\text{Ag}(4)$) and site II' ($\text{Ag}(3)$) is $16 + 16 = 32$, so the S6Rs are fully occupied and simultaneous occupancy is readily avoided.

Finally, eight Ag^+ ions occupy two different III' sites, $\text{Ag}(5)$ and $\text{Ag}(6)$, in the supercage with occupancies of 6 and 2, respectively. The $\text{Ag}(5)\text{--O}(4)$, $\text{Ag}(5)\text{--O}(4')$, $\text{Ag}(6)\text{--O}(1)$, and $\text{Ag}(6)\text{--O}(4)$ distances are imprecise: 2.54(3), 2.64(3), 2.25(7), and 2.82(7) Å, respectively.

Only 86 silver atoms or ions were found per unit cell. The remaining six Ag^+ ions per unit cell were reduced during dehydration and have migrated out of the zeolite framework to form small silver crystallites visible on the surface of the zeolite single crystal.

In this structure, the Ag atoms or ions are found at seven sites: I, I', another I', II, II', III', and another III'. Dehydration of $\text{Ag}_{92}\text{-X}$ in the absence of O_2 gas has apparently led to the formation of $(4 \times 8) + (4 \times 4) = 48$ partially reduced Ag^{z+} ions ($z < 1$) at the two I' and the one II' sites. The cationic clusters Ag_8^{n+} ($n < 8$) and Ag_4^{m+} ($m < 4$) have formed with equal populations in the sodalite cavities; each sodalite cavity hosts a cluster. Perhaps n is four, although two and six are reasonable, and m is two. However the bond lengths in these two clusters are nearly the same, indicating a similar degree of reduction, and this suggests that $n = 4$ and $m = 2$ with each cluster having a charge equal to half of its atomicity.

A Related Structure. Recently, the crystal structure of $\text{Ag}_{92}\text{Si}_{100}\text{Al}_{92}\text{O}_{384}$ dehydrated in flowing oxygen at 360 °C, following by evacuation at 400 °C and 2×10^{-6} Torr for only 2 h, was reported.¹³ That structure is very different from that of crystal 2. Two hours at 400 °C in the absence of oxygen¹³ has clearly produced much less Ag^+ reduction than has 2 days at 400 °C without oxygen gas (crystal 2). In that previously reported structure,¹³ Ag ions or atoms were found at eight crystallographic sites: three Ag^+ ions are at site I, 26 Ag^+ ions

and six Ag^0 atoms are at two I' sites in the sodalite cavities (filling site I'), 32 Ag^+ ions fill site II as in crystal 1, two Ag^0 atoms are on 2-fold axes in the sodalite cavity, and 23 Ag^+ ions occupy three different III' sites. Only six sites are occupied in crystal 2. In that previously reported structure,¹³ the 26 Ag^+ ions at site I' bond weakly in pairs (3.224(3) Å); in crystal 2, the Ag–Ag contact distances are much longer, 3.412(2) and 3.687(9) Å. In that previously reported structure,¹³ three linear Ag_3^+ clusters per unit cell with atoms at sites I', I, and I' lie along 3-fold axes, and two bent (168(2)°) Ag_3^{2+} clusters per unit cell are in the sodalite cavities. The 32 site-II Ag^+ ions in the previous crystal¹³ occupy two different positions in crystal 2, 16 at site II' and 16 at site II.

The increased reaction time that was given to crystal 2 has allowed more Ag atoms to be generated so that larger and more symmetric cationic clusters could form. Only in crystal 2 have excess silver atoms been generated; they migrated out of the zeolite framework to form silver crystallites on the surface of zeolite crystal. The Ag_8^{n+} and Ag_4^{m+} clusters in crystal 2 have short Ag–Ag distances (2.705(6) Å and 2.622(14)/2.749(13) Å, respectively), indicating that these Ag species are more reduced than the former cationic Ag_3 clusters,¹³ the Ag–Ag distances of which are 3.156(5) and 3.224(3) Å, respectively.

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Supporting Information Available: Tables of calculated and observed structure factors. This information is available free of charge via the Internet at <http://pubs.acs.org>.

Note Added after Print Publication. This paper was published on the Web 6/25/2003 and in the July 24, 2003, issue with two errors on p 6944, column one, line 21. The line should read, “ions ($z < 1$) at the two I' and the one II' sites. The cationic clusters”. The electronic version was corrected and reposted to

the Web issue on 8/26/2003. An Addition and Correction appears in the September, 18, 2003, issue (Vol. 107, No. 37).

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