

Three Crystal Structures of Dehydrated $Ag_{12-x}Na_x-A$ ($x= 4, 6, \text{ and } 8$) Treated With Cesium Vapor

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탈수한 $Ag_{12-x}Na_x-A$ ($x = 4, 6, \text{ 및 } 8$)를 세슘 증기로 처리한 세가지 결정구조

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요 약

Ag^+ 이온이 부분적으로 치환된 3가지 제올라이트 $A(Ag_4Na_8-A, Ag_6Na_6-A$ 및 $Ag_8Na_4-A)$ 를 완전히 탈수한 후 $280^\circ C$ 에서 24시간동안 약 0.1 Torr의 Cs증기로 처리하였다. 이들의 결정구조는 $22(1)^\circ C$ 에서 입방공간군 $Pm\bar{3}m$ (단위세포상수 a 가 각각 $12.321(3) \text{ \AA}$, $12.295(1) \text{ \AA}$ 및 $12.380(7) \text{ \AA}$)를 사용하여 단결정 X-선회절법으로 해석하였다. 이들 세가지 구조에서 Cs^+ 이온은 각각 서로 다른 4개의 결정학적 위치에서 발견되었다. 단위세포당 3개의

Cs^+ 이온은 8-링 중심에 위치하고, 약 6.9-7.3개의 Cs^+ 이온은 큰 동공의 6-링과 마주보는 위치에 있는 3회 회전축상에서 발견되었다. 그리고 약 2.17-2.74개의 Cs^+ 이온은 소다라이트 동공내에서 발견되며 약 0.5-1.0개의 Cs^+ 이온은 4-링과 마주보는 곳에 위치한다. 또한 이들 구조에서 단위세포당 각각 1.88(5), 2.30(3) 및 5.28(10)개의 Ag^0 종이 존재하며 이들은 큰동공의 중심에서 헥사실버 클러스터를 형성한다. 8-링위치가 Cs^+ 이온으로 모두 차있어서 Ag^0 가 골조밖으로 이동하는 것을 막을 수 있다. 각각의 헥사실버 클러스터는 서로 다른 좌표에 위치하는 14개의 Cs^+ 이온에 의

해 안정화된다. 이들 구조에서 발견되는 약 12.35-13.49개의 Cs^+ 이온들은 Cs^0 의 흡착이 일어나 제올라이트 기본 골격에 있는 음이온 전하와 균형을 맞출 수 있는 12개의 Cs^+ 이온 이상의 이온 또는 원자로 존재하고 있다. Cs 의 배열은 다음과 같은 두가지 배열로 쉽게 설명할 수 있다. 일부는 2개의 Cs^+ 이온이 소다라이트 동공내에 있는 6-링과 마주보는 곳에 위치하고 큰동공내에는 6개의 Cs^+ 이온이 6-링 근처에 위치하며 1개는 4-링 근처에 위치한다. 그 나머지는 소다라이트 동공내에 위치하는 3개의 Cs^+ 이온과 한번의 길이를 3.52 Å로 갖는 삼각형을 형성한 후 6-링을 통하여 큰 동공 내에 위치한 3개의 Cs 원자와 결합하게 되므로 $3m$ (C_{3v})의 대칭구조를 갖는 $(Cs_6)^{4+}$ 클러스터를 형성한다. 그 밖의 5개 Cs^+ 이온은 비어있는 큰동공의 6-링에 위치한다.

Abstract

Three fully dehydrated partially Ag-exchanged zeolite-A (Ag_4Na_8 -A, Ag_6Na_6 -A, and Ag_8Na_4 -A) were treated at 280 °C with 0.1 Torr Cs vapor for 24h. Their structures were determined by single-crystal X-ray diffraction methods in the space group $Pm\bar{3}m$ ($a = 12.321(3)$ Å, $12.295(1)$ Å, and $12.380(7)$ Å, respectively) at 21(1) °C. In these structures, Cs species are found at four different crystallographic sites: 3 Cs^+ ions per unit cell are located at 8-ring centers, ca. 6.92-7.28 Cs^+ ions are found opposite 6-rings on threefold axes in the large cavity, ca. 2.17-2.74 Cs^+ ions are found on threefold axes in the sodalite unit, and ca. 0.5-1.0 Cs^+ ion lie opposite 4-rings. Also, in each structure, the numbers of Ag atoms per unit cell are 1.88(5), 2.30(3), and 5.28(10), respectively, and these are likely to form hexasilver clusters at the centers of the large cavities. The Cs^+ ions, by blocking 8-rings, may have prevented silver from migrating out of the structure. Each hexasilver cluster is stabilized by coordination to up to 14 Cs^+ ions. Also, in these structures ca. 12.35-13.49 Cs^+ ions and/or atoms are found per unit cell, more than the 12 Cs^+ ions need to balance the anionic charge of the zeolite framework, suggesting that the sorption of

Cs^0 has occurred. Beyond that, the fractional occupancies observed are most simply explained by two kinds of unit-cell arrangements. In one part, two Cs^+ ions are in the sodalite unit near opposite 6-oxygen rings, six are in the large cavity near 6-oxygen rings, and one is in the large cavity near a 4-oxygen ring. In the other part, three Cs^+ ions in the sodalite cavity (forming a triangle 3.52 Å on an edge) bind through a six-oxygen ring three Cs species in the large cavity to give a $(Cs_6)^{4+}$ cluster of symmetry $3m$ (C_{3v}) and five additional Cs^+ ions fill the remaining large-cavity six-oxygen ring site.

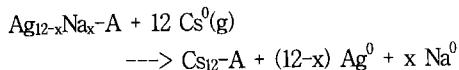
Introduction

Ag^+ ions in zeolite A can be easily reduced by H_2 , and reduced Ag atoms or cluster can be readily reoxidized to Ag^+ by O_2 .¹ An $(Ag_6)^{3+}$ cluster was found crystallographically in the large cavity of partially Ag^+ -exchanged zeolite A treated with H_2 .

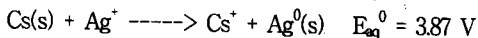
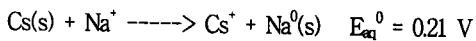
The neutral cluster $(Ag_6)^0$, stabilized by coordination to 8 Ag^+ ions, has been found by X-ray diffraction methods.²⁻⁴ This cluster may alternatively be viewed as $(Ag_{14})^{8+}$. Hermerschnidt and Haul also identified Ag_n^{n+} ($n < 6$) clusters in the sodalite cavities of dehydrated Ag-A zeolite by EPR spectroscopy.⁵

In 1987, Seff and Heo succeeded in preparing fully dehydrated, fully Cs^+ -exchanged zeolite A by the reduction of all Na^+ ions in Na_{12} -A with cesium vapor.^{6,7} Its formula, however, is not Cs_{12} -A but Cs_{12} -A.1/2Cs, which contain 0.5 extra cesium atom per unit cell. This combines with Cs^+ ions to form cationic cesium clusters, $(Cs_4)^{3+}$.^{6,7}

This work was initiated with the hope that the intrazeolitic redox potential for the reaction



would be positive enough to ensure complete exchange. The E^0 values, not involving the zeolite, are easily calculated.⁸



The resulting material would be interesting because the volume of exchangeable cations would be large and some extra Cs^0 atoms may be present, forming Cs clusters. However, in this experiment, the reduced silver may not be able to diffuse to the surface of zeolite because of the blockage of the 8-windows by the large Cs^+ ions. By such trapping, some new, perhaps larger, clusters might form and be identified. Furthermore, because of the atomic size and the high scattering powers of Cs^+ and Ag^+ , precise and reliable crystallographic determinations should be easy to achieve.

Experimental section

Complete Ag^+ exchange of zeolite 4A powder is accomplished by a static method: 0.2 grams of zeolite 4A (Union Carbide, Lot 494107701161) was allowed to exchange at $24^\circ C$ with a 6-fold excess of 0.05N $AgNO_3$, and the solution was agitated periodically. Each day, the supernatant solution was decanted and a fresh aliquot of 0.05 N $AgNO_3$ was added. After 7 days, the zeolite powder was filtered and dried. For the preparation of $Ag_{12-x}Na_x-A$ ($x = 4, 6$, and 8) samples, $Ag_{12}-A$ and $Na_{12}-A$ were mixed in 2.65 : 1, 4.60 : 1, and 6.25 : 1 weight ratio, respectively. A few large single crystals of zeolite 4A, which had been prepared by Charnell's method⁹⁾, were added to these powder mixtures, with enough water to submerge all solid particles so that the composition of the large crystals would be Ag_8Na_4-A , Ag_6Na_6-A , and Ag_4Na_8-A at equilibrium. After 3 days, the water was allowed to evaporate in air at room temperature.

A single crystal 0.08 mm on an edge was selected and lodged in a fine Pyrex capillary. The hydrated, partially Ag^+ -exchanged crystal was dehydrated for 48h at $380^\circ C$ and 2×10^{-6} Torr. Cesium vapor was introduced by distillation from a side-arm break-seal

ample to the Pyrex-tube extension of the crystal-containing capillary. This glass reaction vessel was then sealed off under vacuum and placed within a pair of cylindrical horizontal ovens, axes collinear attached. The oven about crystal always maintained at a higher temperature than the cesium metal so that cesium would not distill onto the crystal.

Each crystal was allowed to react with 0.1 Torr of $Cs(g)$ at $280^\circ C$ for 24h. The crystal was then sealed off from its reaction vessel by torch after cooling to room temperature. Microscopic examination showed that all these crystals had become metallic black.

The space group $Pm\bar{3}m$ (no systematic absences) was used through this work for reasons discussed previously.^{10,11)} Preliminary crystallographic experiments and subsequent data collection were performed with a Enraf-Nonius 4-circle computer-controlled CAD4 diffractometer, equipped with a graphite monochromator, a pulse-height analyzer, and a Micro VAX 3100 computer. Molybdenum radiation ($K\alpha_1 = 0.70930 \text{ \AA}$, $K\alpha_2 = 0.71359 \text{ \AA}$) was used for all experiments. In each case, the cell constant, $a = 12.321(3) \text{ \AA}$, $12.295(1) \text{ \AA}$, and $12.380(7) \text{ \AA}$ for crystals 1, 2, and 3, respectively, were determined by a least-squares treatment of 24 intense reflections in the range of $20^\circ < 2\theta < 30^\circ$.

Reflections from two intensity-equivalent regions of reciprocal space (hkl , $0 \leq h \leq k \leq l$; klh , $0 \leq k \leq l \leq h$) were examined by using the $w-2\theta$ scan technique. The data were collected using variable scan speeds. Most reflections were observed at slow scan speeds, from 0.39 to $0.50 \text{ deg min}^{-1}$ in w . The intensities of three reflections in diverse regions of reciprocal space were recorded every 3h to monitor crystal and instrument stability. Only small, random fluctuations of these check reflections were noted during the course of data collection. For each region of reciprocal space, the intensities of all lattice points for which $2\theta < 70^\circ$ were recorded. The raw data from each region were corrected for Lorentz and polarization effects including beam monochromatization. The reduced intensities were merged, and the resultant estimated standard deviations

were assigned to each averaged reflection by the computer programs, PAINT and WEIGHT.¹²⁾ Absorption corrections (μ_r ca. 0.40) were judged to be negligible for all crystals.¹³⁾ Of the 892, 894, and 890 pairs of reflections for crystal 1, 2, and 3 respectively, only 177, 199, and 163 pairs, respectively, for which $I > 3\sigma(I)$ were used in subsequent structure determinations.

Structure Determination

Crystal 1. (Dehydrated Ag_4Na_8-A treated with Cs(g)) Full-matrix least-squares refinement was

initiated with atomic parameters of the framework atoms (Si, Al), O(1), O(2), and O(3) of dehydrated $Cs_{7.3}Ag_{47}-A$.¹³⁾

Anisotropic refinement of the framework atoms converged to unweighted R1 index, $(\sum |F_o - |F_c||) / \sum F_o$, of 0.45 and weighted R2 index, $(\sum w(F_o - |F_c|)^2 / \sum wF_o^2)^{1/2}$, of 0.56.

A subsequent Fourier synthesis revealed three large peaks at (0.0, 0.5, 0.5) of height $34.2(2) e\text{\AA}^{-3}$, and (0.28, 0.28, 0.28) of height $48.3(1) e\text{\AA}^{-3}$, and (0.10, 0.10, 0.10) of height $12.3(2) e\text{\AA}^{-3}$.

Table 1. Positional, Thermal,^a and Occupancy Parameters of $Ag_{12-x}Na_x-A$ reacting with Cs Vapor^b

Crystal 1											
Atom	Wyc. Pos	x	y	z	β_{11}^c or β_{iso}^d	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	^e Occupancy varied fixed
(Si, Al)	24(K)	0	1844(7)	3733(7)	39(6)	24(5)	13(5)	0	0	10(10)	24.0 ^f
0(1)	12(h)	0	2260(30)	5000	40(20)	60(30)	59(1)	0	0	0	12.0
0(2)	12(h)	0	2930(20)	2930(20)	10(20)	50(10)	50(10)	0	0	80(40)	12.0
0(3)	24(m)	1120(10)	1120(10)	3460(20)	41(9)	41(9)	40(20)	20(30)	10(20)	10(20)	24.0
Cs(1)	3(c)	0	5000	5000	150(10)	81(5)	51(5)	0	0	0	3.00
Cs(2)	8(g)	2790(30)	2790(30)	2790(30)	61(2)	61(2)	61(2)	14(6)	14(6)	14(6)	6.92(5)
Cs(3)	8(g)	1000(10)	1000(10)	1000(10)	120(10)	120(10)	120(10)	-30(20)	-30(20)	-30(20)	2.17(5)
Cs(4)	12(l)	2230(10)	2230(10)	5000	7.0(Fixed) ^d						0.26(5)
Ag(1)	6(f)	3360(20)	5000	5000	130(30)	110(10)	110(10)	0	0	0	1.88(6)
Crystal 2											
(Si, Al)	24(K)	0	1853(4)	3722(4)	16(3)	16(3)	17(3)	0	0	11(6)	24.0 ^f
0(1)	12(h)	0	2250(10)	5000	90(20)	30(10)	20(10)	0	0	0	12.0
0(2)	12(h)	0	2935(9)	2935(9)	30(10)	32(7)	32(7)	0	0	10(10)	12.0
0(3)	24(m)	1120(5)	1120(9)	3429(5)	36(5)	32(9)	32(9)	10(10)	10(10)	10(10)	24.0
Cs(1)	3(c)	0	5000	5000	144(6)	67(2)	67(2)	0	0	0	3.00
Cs(2)	8(g)	2794(1)	2794(1)	2794(1)	52(7)	52(7)	52(7)	9(2)	9(2)	9(2)	7.28(3)
Cs(3)	8(g)	1013(4)	1013(4)	1013(4)	133(5)	133(5)	133(5)	-60(10)	-60(10)	-60(10)	2.74(3)
Cs(4)	12(l)	2440(40)	2440(40)	5000	7.0(Fixed) ^d						0.47(4)
Ag(1)	6(f)	3370(10)	5000	5000	240(20)	105(7)	105(7)	0	0	0	2.30(3)
Crystal 3											
Atom	Wyc. Pos	x	y	z	β_{11}^c or β_{iso}^d	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	^e Occupancy varied fixed
(Si, Al)	24(K)	0	1800(20)	3710(10)	30(10)	40(10)	10(10)	0	0	-20(20)	24.0 ^f
0(1)	12(h)	0	2320(50)	5000	50(70)	10(60)	69(30)	0	0	0	12.0
0(2)	12(h)	0	2860(40)	2860(40)	40(50)	40(20)	40(20)	0	0	70(40)	12.0
0(3)	24(m)	1120(20)	1120(20)	3520(40)	60(30)	60(30)	80(40)	20(6)	30(10)	30(10)	24.0
Cs(1)	3(c)	0	5000	5000	200(30)	80(10)	60(10)	0	0	0	3.00
Cs(2)	8(g)	2825(6)	2825(6)	2825(6)	90(4)	90(4)	90(4)	20(10)	20(10)	20(10)	7.10(10)
Cs(3)	8(g)	1060(10)	1060(10)	1060(10)	40(10)	40(10)	40(10)	-30(20)	-30(20)	-30(20)	2.40(8)
Cs(4)	12(l)	2300(80)	2300(80)	5000	7.0(Fixed) ^d						0.83(13)
Ag(1)	6(f)	3350(30)	5000	5000	260(20)	270(30)	2710(30)	0	0	0	5.28(10)

^aPositional and anisotropic thermal parameters are Given X 10⁴. Numbers in Parentheses are the esd's in the units of the least significant digit given for the corresponding Parameter, ^b $Ag_{12-x}Na_x-A$ ($x=4, 6$, and 8) treated with 0.1 Torr of Cs vapor at 280°C for 24h. ^cthe anisotropic temperature factor = $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

^dIsotropic thermal parameters in unit of \AA^2 . ^eOccupancy factors are given as number of atoms or ions per unit cell. (Occupancy for (Si)=12; occupancy for (Al)=12.

Anisotropic refinement of the framework atoms and the Cs⁺ ions at Cs(1), Cs(2), and Cs(3) (see Table I) converged R₁ = 0.100, and R₂ = 0.085 with occupancies 3.06(1), 6.80(5), and 2.92(5) respectively. An ensuing difference Fourier synthesis revealed the positions of Cs species at Cs(4), (0.233, 0.233, 0.5), with peak height 1.95(3) eÅ⁻³, and at Ag(1), (0.334, 0.5, 0.5), with peak height 6.35(2) eÅ⁻³.

Cs(4) peak refined with an unusually large thermal parameter. Therefore, the isotropic thermal parameter of Cs(4) was fixed at the more reasonable value given in Table I. Allowing all occupancies of Cs(i), (i = 1, 2, 3, and 4) and Ag(1), to vary, except that of Cs(1) which was not permitted to exceed 3.0 (its maximum occupancy by symmetry), and allowing all anisotropic thermal parameters to vary, except for that of Cs(4) which was refined isotropically, led to R₁ = 0.080 and R₂ = 0.072 with refined occupancies as given in the last column of Table I.

The largest peak on final difference Fourier function was at (0.0, 0.0, 0.0) with height 0.6(4) eÅ⁻³. This peak was rejected because it was too close (2.24 Å) to Cs species at Cs(3).

Crystal 2. (Dehydrated Ag₆Na₆-A treated with Cs(g)). Using the atomic coordinates from the structure of Crystal 1, simultaneous occupancy, positional, and thermal parameter refinement was initiated. Anisotropic refinement of all positions, except for that of Cs(4), which was refined isotropically, converged quickly to R₁ = 0.051 and R₂ = 0.044. The number of Cs atoms and ions at Cs(1), Cs(2), Cs(3), Cs(4), and Ag(1) refined 3.03(3), 7.26(2), 2.75(3), 0.51(5), and 2.30(3) ions or atoms per unit cell, respectively. The occupancy of Rb(1) was fixed at 3.0, its maximum occupancy by symmetry. The final R values converged at R₁ = 0.050, and R₂ = 0.042.

A final difference Fourier synthesis was featureless except for some residual density (0.8(2) eÅ⁻³) at (0.28, 0.5, 0.5) near Ag(1), deep in the large cavity.

Crystal 3. (Dehydrated Ag₃Na₄-A Treated with

Cs(g)). Using the atomic coordinates from the

Table I. Selected Interatomic Distance (Å) and Angles (deg) of Ag₁₂-XNa_x-A (x=4, 6, and 8) treated with Cs vapor

	Crystal1	Crystal2	Crystal3
Si, Al -O(1)	1.64(1)	1.65(3)	1.72(3)
Si, Al -O(2)	1.66(2)	1.66(1)	1.68(4)
Si, Al -O(3)	1.67(4)	1.67(3)	1.64(2)
Cs(1) -O(1)	3.37(4)	3.38(2)	3.31(6)
Cs(1) -O(2)	3.62(1)	3.59(1)	3.74(3)
Cs(2) -O(2)	3.44(6)	3.44(3)	3.49(6)
Cs(2) -O(3)	3.04(1)	3.01(4)	3.11(2)
Cs(3) -O(2)	3.57(2)	3.56(7)	3.41(3)
Cs(3) -O(3)	3.04(2)	2.98(1)	3.04(5)
Cs(4) -O(1)	2.75(6)	3.00(4)	2.85(4)
Ag(1) -O(1)	5.34(4)	5.54(2)	5.31(5)
Cs(1) -Cs(2)	5.16(2)	5.14(6)	5.17(1)
Cs(1) -Cs(4)	4.40(9)	4.35(3)	4.29(7)
Cs(2) -Cs(2)	5.44(6)	5.42(5)	5.38(6)
Cs(2) -Cs(3)	3.81(1)	3.79(3)	3.77(4)
Cs(3) -Cs(3)	3.49(9)	3.52(2)	3.73(1)
	4.29(2)	4.31(4)	4.57(1)
Ag(1) -Cs(1)	4.13(3)	4.39(2)	4.15(4)
Ag(1) -Cs(2)	3.91(4)	3.95(4)	3.86(7)
Ag(1) -Cs(4)	5.35(9)	5.22(3)	5.14(7)
Ag(1) -Ag(1)	2.87(3)	2.90(2)	2.88(4)

structure of crystal 1, simultaneous occupancy, positional, and thermal parameter refinement was done. Anisotropic refinement for all positions except for that of Cs(4), which was refined isotropically, converged to R₁ = 0.077 and R₂ = 0.074. Occupancy refinement converged 3.08(3), 6.98(10), 2.41(8), 0.90(14), and 5.24(10) for Cs(1), Cs(2), Cs(3), Cs(4), and Ag(1) (see Table I), respectively. The occupancy at Cs(1) was fixed at 3.0 as before. The final R values converged at R₁ = 0.076 and R₂ = 0.075.

The largest peak on final difference Fourier function was at (0, 0, 0) with height 0.62(3) eÅ⁻³. This peak was rejected because it was too close (2.24 Å) to Cs species at Cs(3). All shifts in the final cycles of least-squares refinement for all three crystals were less than 0.1% of their corresponding standard deviations.

For all structures, the full-matrix least-squares program used minimized $\sum w(F_o - |F_c|)^2$; the weight w of an observation was the reciprocal square of s(F), its standard deviation. Atomic scattering factors for Cs⁺, Ag⁰, O⁻ and (Si,Al)^{1.75+} were used.¹⁴ 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.^{15,16} The final structure parameters and selected interatomic distances

and angles are presented in Table I and II, respectively.

Discussion

In all structures, Cs^+ ions found at four different crystallographic sites (see Table I). The three structures are similar except for the occupancies at the Cs(2), Cs(3), Cs(4), and Ag(1) positions.

In each structure, three Cs^+ ions at Cs(1) fill equipoints of symmetry C_{4h} (D_{4h} in $\text{Pm}\bar{3}m$) at the centers of 8-rings. Each Cs(1) ion is ca. 3.31–3.37 Å from four O(1) oxygens and ca. 3.59–3.74 Å from four O(2)s (see interatomic distances in Table II). These distances are substantially longer than the sum of the ionic radii of O^{2-} and Cs^+ , 3.09 Å. Cs^+ ions were observed at this site in all previous studies of Cs^+ -exchanged zeolite A, with similar long contact distances.^{17–19)}

In the large cavity opposite 6-rings, ca. 6.92(5), 7.28(3), and 7.10(10) Cs^+ ions are found at Cs(2) in crystal 1, 2 and 3, respectively (see Table I). In the sodalite unit opposite 6-rings, 2.92(5), 2.75(3), and 2.41(8) Cs^+ ions, respectively, are found at Cs(3). The sum of these three fold-axis occupancies at Cs(2) and Cs(3) are 9.78, 10.01, and 9.39 for crystal 1, 2, and 3, respectively (see Table I). If the Cs species at Cs(2) and Cs(3) are all ions, this sum should not exceed eight; otherwise an unacceptably short distance (3.80 Å) between Cs(2) and Cs(3) would exist. By difference, therefore, at least ca. 1.4–2.0 Å of these very close Cs(2)–Cs(3) contact distance must exist. Also, the presence of more than two Cs(3) species per sodalite unit requires ca. 3.8 Å Cs(3)–Cs(3) contacts.

Each ion at Cs(2) is ca. 3.08(3) Å from the three O(3) oxygens of its six-oxygen ring and ca. 1.92(3) Å from the (111) plane at O(3). Cs(3) is correspondingly ca. 3.02(3) Å from three O(3) oxygens and recessed ca. 1.95(3) Å into sodalite cavity from the (111) plane of three O(3)s (see Table III).

In each structure, the ion at Cs(4) lie opposite to a

Table II. Deviation of atom(Å) from the (111) plane at O(3) of $\text{Ag}_{12-x}\text{Na}_x\text{-A}(X=4, 6 \text{ and } 8)$ treated with Cs vapor.^a

	Crystal 1	Crystal 2	Crystal 3
O(2)	0.10(1)	0.07(1)	-0.05(6)
Cs(2)	1.90(3)	1.89(3)	1.94(5)
Cs(3)	-1.90(9)	-1.97(3)	-1.82(6)
Ag(1)	5.44(9)	5.43(7)	5.46(7)

^aA negative deviation indicates that the atom lies on the same side of the Plane as the origin

four-oxygen ring. This Cs^+ ion is somewhat closer, ca. 2.87(6) Å, to O(1) oxygens than the sum of the conventional ionic radii, 2.99 Å. Such short bonds are common in dehydrated zeolite A structures which contain large monovalent cations, perhaps because of their unusually low occupancy numbers within the zeolite.

The center of the large cavity is occupied by Ag atoms produced by the reduction of Ag^+ by Cs^0 . The sum of the Cs(i) (i = 1, 2, 3, and 4) and Ag(1) occupancies in crystal 1, 2, and 3 (see Table I) are 14.2(3), 15.7(9), and 18.6(1), respectively. The unit cells clearly contain more metal species than the approximately 12 monovalent cations which are required to balance the anionic charge of the zeolite framework, which is estimated to be -11.75^{20} to -12^{11} per unit cell. Therefore about two to six metal atoms must exist per unit cell. Those may be present as isolated atoms or neutral clusters or they may associate with cations to form cationic clusters.

Table IV. Inferred Unit Cell Compositions for Crystal 1, 2, and 3.

Positions of cations and atoms	crystal1			crystal2			crystal3		
	50%	30%	20%	60%	40%	50%	40%	10%	
8-ring, Cs(1)	3	3	3	3	3	3	3	3	
6-ring, Cs(2) (large-cavity side)	6	8	8	8	6	6	8	8	
6-ring, Cs(3) (sodalite Side) opposite 4-ring Cs(4)	2	3	3	3	2	2	3	3	
Center of large cavity, Ag(1)	1	0	0	0	1	1	0	0	
	0	6	0	0	6	6	6	0	

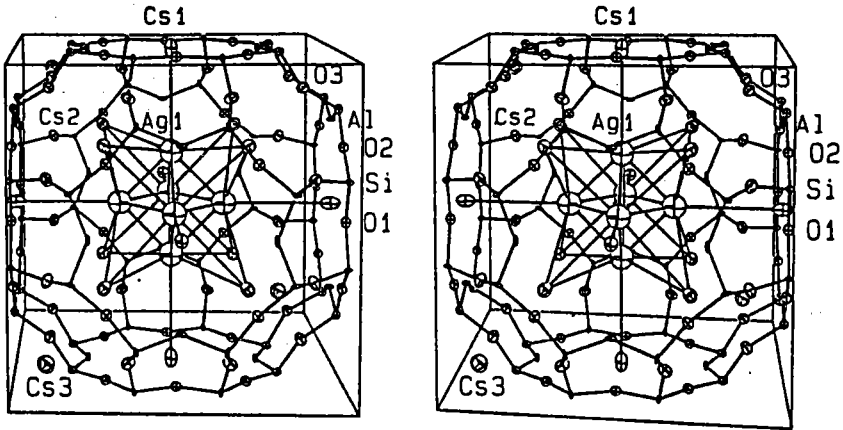


Figure 1. A stereoview of the large cavity of dehydrated Ag₃Na₄-A treated with Cs vapor. 3 Cs⁺ ions at Cs(1), 8 Cs⁺ ions at Cs(2), 3 Cs⁺ ions at Cs(2), 3 Cs species Cs(3), and one octahedral Ag₆ molecule are shown. About 40% of the unit cells may have this arrangement. Ellipsoids of 25% probability are used.

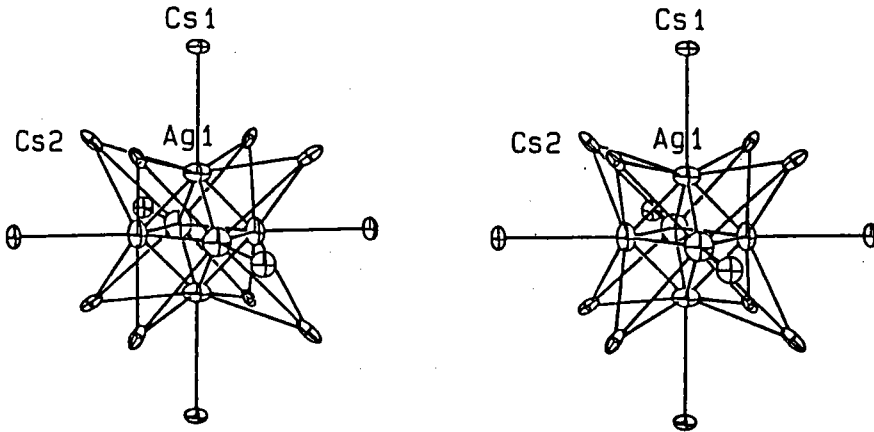


Figure 2. The octahedral Ag₆ molecule, stabilized by coordination to 3 Cs⁺ ions at Cs(1), 8 Cs(2) are shown. Ellipsoids of 25% probability are used.

The distances from Ag(1) to Cs(1) and Cs(2) are ca. 4.23 Å and ca. 3.90 Å, respectively. The relatively large thermal ellipsoids of the Ag atoms at Ag(1) indicate that the hexasilver cluster is loosely held at its position.

To maximize the number of favorable interactions each structure may be viewed as composed of several different unit cell composition as Table IV. For example, about 30% of the unit of crystal 1 may contain

three Cs ions at Cs(1), eight Cs⁺ ions at Cs(2), and three Cs species at Cs(3). The Ag atoms at Ag(1) would form a hexasilver cluster which would be stabilized by association with eight ions at Cs(2) and three ions at Cs(1). (see Figure 1) The formula of an individual metal cluster may be viewed as (Ag₆)⁰(Cs⁰)₂(Cs⁺)₁₂ (see Figure 2). About 50% of the unit cell may contain six Cs(2) ions associated with their six-oxygen rings on their large-cavity sides, two

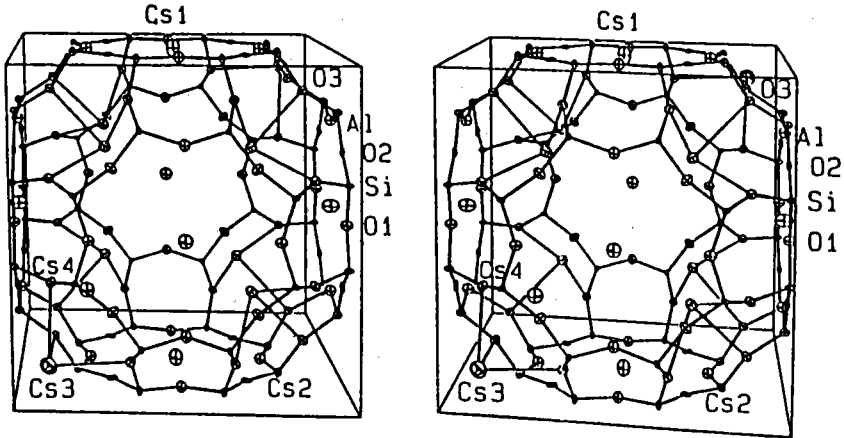


Figure 3. A stereoview of the large cavity of dehydrated Ag_4Na_8-A treated with Cs vapor. 3 Cs ions at Cs(1), 6 Cs^+ ions at Cs(2), 2 Cs^+ ions at Cs(3), and one Cs species at Cs(4) are shown. About 50% of the unit cells may have this arrangement. Ellipsoids of 25% probability are used.

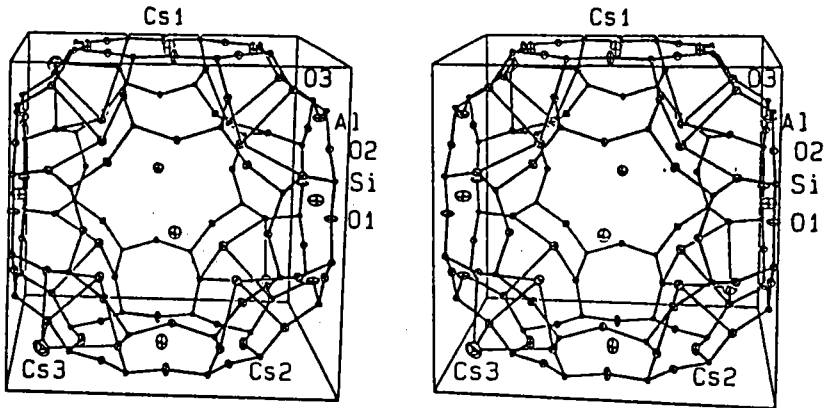


Figure 4. A stereoview of the large dehydrated Ag_4Na_8-A treated with Cs vapor. 3 Cs^+ ions at Cs(1), 8 Cs^+ ions at Cs(2), and 3 Cs^+ ions at Cs(3) are shown. About 60% of the unit cells may have this arrangement. Ellipsoids of 25% probability.

Cs^+ ions at Cs(3), and one Cs ion at Cs(4) (see Figure 3). And remaining cell have contain three Cs^+ ions at Cs(1), eight Cs ions at Cs(2), and three Cs species at Cs(3). (Figure 4) These eight are better associated with sodalite units containing the Cs(3) triangle, to allow further electron delocalization, than with sodalite units which contain three Cs(3) cations, where the very short 3.79 Å approach between Cs(2) and Cs(3) would be naked, that is, unameliorated by excess (bonding) electron density. (see Figure 5) It follows that this

sodalite unit has, associated with its six-oxygen rings, 11(3 + 8) Cs species, 9 of those may be counted as Cs^+ (to balance framework charge) and two as Cs^0 . The two electrons from these Cs^0 's per sodalite unit must be delocalized over the shortest Cs-Cs contacts in the structure, those among the three Cs(3)'s in the sodalite cavity and the three Cs(2)'s (of the eight in the large-cavities adjacent to the sodalite unit) nearest to these Cs(3)'s, to give the $(Cs_6)^{4+}$ cluster shown in Figure 6.

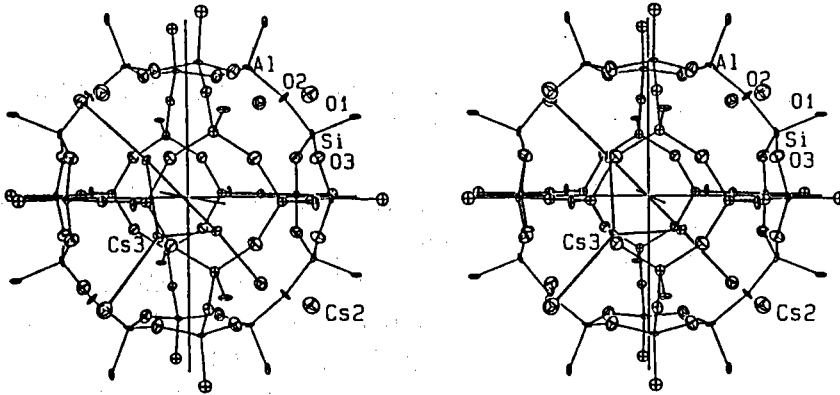


Figure 5. The $(Cs_3)^{4+}$ cluster. It has $3m (C_3)$ symmetry. An $Cs(2)$ - $Cs(3)$ bond makes an angle of 160.53° (by symmetry) with the central $Cs(3)$ plane. Ellipsoids of 20% probability are used.

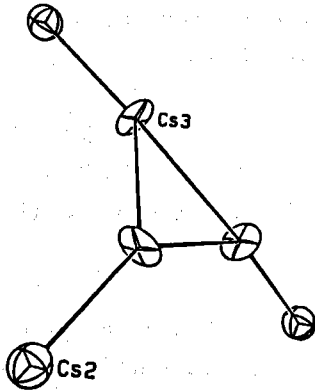


Figure 6. A stereoview of about 60% of the sodalite cavities in dehydrated partially Ag^+ -exchanged zeolite A exposed to excess $Cs(g)$. Each $Cs(3)$ of the central triangle of the cluster interacts further with an $Cs(2)$ to form the complete $(Cs_3)^{4+}$ cluster. Ellipsoids of 20% probability are used.

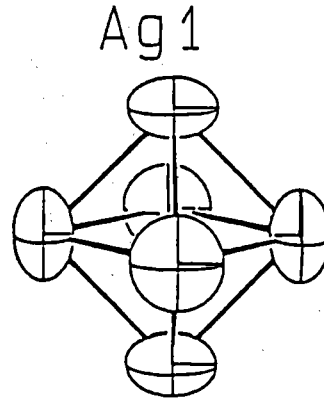


Figure 7. The octahedral Ag_6 molecule is shown using ellipsoids of 50% probability.

The distance between $Ag(1)$ and its nearest framework oxygens, two at $O(1)$, is very much longer ($Ag(1)$ - $O(1)$ = ca. 5.39 Å) than the sum of the approximate ionic radii, 2.58 Å.²¹⁾ This indicates that the species at $Ag(1)$ must be Ag^0 and not Ag^+ . The shortest distance between $Ag(1)$ and $Ag(1)$, ca. 2.87 Å, which must exist whenever more than two silver species at $Ag(1)$ are present per unit cell, is far too short to be an unmoderated Ag^+ - Ag^+ distance. This $Ag(1)$ - $Ag(1)$

distance is close to Ag^0 - Ag^0 distance, 2.89 Å,²¹⁾ in silver metal. If the $Ag(1)$ equipoints were filled in fraction of the large cavities closest packed clusters of six silver atoms would exist in all three structures. The hexasilver molecule would be octahedral and would show the full symmetry of its site, O_h at center of the large cavity. The occupancy at $Ag(1)$ in crystal 1, 2, and 3 is 1.88(6), 2.30(3), and 5.28(10). In crystal 3, $Ag(1)$ occupied 5.28(10) atoms per unit cell, higher by

ca. 1.3 than had been achieved for the sodalite Ag_6 cluster in previous studies.³⁾ This indicates that pentasilver may exist in almost unit cells as an alternative to the hexasilver cluster. However, it is unlikely that the less symmetric pentasilver with eight Ag-Ag contact (1.6 per atom). It would be more stable than hexasilver with 12 such contacts (2.0 per atom), and that it would occupy a site of O_h symmetry. (see Figure 7)

The present work is different from the previous one, in which the crystal of dehydrated Ag_6Na_6-A was treated with 0.1 Torr of Cs(g) at 250°C for 12h. In this work, Ag^+ ions were partially reduced and an $(Ag_5)^+$ cluster was present in 64% of large cavity.²⁾

Without a stabilization mechanism, metal clusters like hexasilver would generally not be retained within the zeolite structure. Because a mechanism associated with the ions at Cs(1) and Cs(2) is to be detected, it is reasonable to accept the fact that atoms of silver have formed and have been retained within zeolite A. The structure and symmetry of this hexasilver cluster could be exactly found at the center of sodalite unit in partially decomposed and fully dehydrated Ag^+ -exchanged zeolite A.²³⁾

Acknowledgement

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