

- LUMO were 0.59, 0.15 and 0.58, 0.57 for OCH<sub>2</sub>Cl and OSO<sub>2</sub>OCl respectively.
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## Crystal Structure of Fully Dehydrated Partially Ag<sup>+</sup>-Exchanged Zeolite 4A, Ag<sub>7.6</sub>Na<sub>4.4</sub>-A. Ag<sup>+</sup> Ions Prefer 6-Ring Sites. One Ag<sup>+</sup> Ion is Reduced

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The structure of partially Ag<sup>+</sup>-exchanged zeolite 4A, Ag<sub>7.6</sub>Na<sub>4.4</sub>-A, vacuum dehydrated at 370°C, has been determined by single-crystal x-ray diffraction techniques in the cubic space group, *Pm3m* ( $a = 12.311(1)\text{\AA}$ ) at 24(1)°C. The structure was refined to the final error indices  $R_1 = R_2$  (weighted) = 0.064 using 266 independent reflections for which  $I_o > 3\sigma(I_o)$ . Three Na<sup>+</sup> ions occupy the 3 8-ring sites, and the remaining ions, 1.4 Na<sup>+</sup> and 6.6 Ag<sup>+</sup>, fill the 8 6-ring sites; each Ag<sup>+</sup> ion is nearly in the [111] plane of its 3 O(3) ligands, and each Na<sup>+</sup> ion is 0.9Å from its corresponding plane, on the large-cavity side. One reduced silver atom per unit cell was found inside the sodalite unit. It was presumably formed from the reduction of a Ag<sup>+</sup> ion by an oxide ion of a residual water molecule or of the zeolite framework. It may be present as a hexasilver cluster in 1/6 of the sodalite units, or, most attractively among several alternatives, as an isolated Ag atom coordinated to 4 Ag ions in each sodalite unit to give (Ag<sub>5</sub>)<sup>+</sup>, symmetry  $4mm$ .

### Introduction

Ag<sup>+</sup> ions in zeolite A can be reduced by heating,<sup>1,2</sup> by reaction with reducing agents,<sup>3</sup> or by the sorption of metal atoms.<sup>4</sup> (Many reports of the reduction of Ag<sup>+</sup> by these methods in other zeolites can be found.) Recently the structures of dehydrated Ag<sub>7.6</sub>Na<sub>4.4</sub>-A treated with H<sub>2</sub> at room temperature and at 330°C were determined in an effort to learn more about the reduction of silver ions in partially Ag<sup>+</sup>-exchanged zeolite A.<sup>3,5</sup> In the structure of dehydrated Ag<sub>6</sub>Na<sub>6</sub>-A<sup>3,6</sup> treated with 50 torr of H<sub>2</sub> at room temperature, 1.27 (Ag<sub>3</sub>)<sup>+</sup> clusters and 0.7 (Ag<sub>3</sub>)<sup>+</sup> clusters per unit cell were found in the large cavity. In the structure of Na<sub>7.4</sub>Ag<sub>4.6</sub>-A, vacuum dehydrated and treated with H<sub>2</sub> at 350°C, (Ag<sub>6</sub>)<sup>+</sup> clusters were present in the large cavity.<sup>5</sup>

Schöller *et al.* investigated the influence of monovalent cations in different positions in zeolite 4A on the diffusivity of trans-2-butene.<sup>7</sup> They concluded that Ag<sup>+</sup> ions preferentially occupy 6-ring centers and that Na<sup>+</sup> ions prefer 8-ring sites.<sup>8</sup> Similar results were obtained by Nitta *et al.*,<sup>9</sup> who studied the site selectivity of Ag<sup>+</sup> ions in dehydrated Ag<sub>6</sub>Na<sub>6</sub>-A by calculating cation-lattice interaction energies and charge-transfer stabilization energies for Ag<sup>+</sup> and Na<sup>+</sup> cations in 6-ring and in 8-ring sites.

This work was done to determine the cation distribution crystallographically, to see whether complete dehydration of Ag<sub>7.6</sub>Na<sub>4.4</sub>-A could be achieved at 370°C without generating Ag atoms, and to learn the structure for comparison with others of similar composition evacuated at other temperatures or treated with H<sub>2</sub>.

## Experimental

First, the complete  $Ag^+$ -exchange of a sample of zeolite 4A powder was accomplished by a static method. Two grams of zeolite 4A (Union Carbide, Lot no.: 494107701161) were allowed to exchange at 24°C with a 7-fold excess of 0.1 N  $AgNO_3$ , and the mixture was agitated periodically. Each day, the supernatant solution was decanted and a fresh aliquot of 0.1 N  $AgNO_3$  was added. After 8 days, the zeolite,  $Ag_{12}A$ ,<sup>6</sup> was filtered and dried.

Samples of  $Ag_{12}A$  and  $Na_{12}A$  were mixed in a 2:1 mole ratio, neglecting water contents. To this mixture were added a few large single crystals of zeolite A which had been prepared by Charnell's method,<sup>10</sup> with enough water to submerge all solid particles so that at equilibrium the large crystals would have the composition  $Ag_6Na_6A$ . After 3 days, the water was allowed to evaporate in air at room temperature.

A single crystal, 80  $\mu m$  on an edge, was selected and lodged in a fine glass capillary. The clear colorless hydrated partially  $Ag^+$ -exchanged crystal was dehydrated for 48 hours at 370°C and  $1.5 \times 10^{-6}$  torr, and was then sealed off in its capillary by torch. Microscopic examination showed that the crystal was gray, neither black nor silvered.

Diffraction intensities were subsequently collected at 24°C. The space group  $Pm\bar{3}m$  (no systematic absences) was used throughout this work for reasons discussed previously.<sup>8,11</sup> A Syntex 4-circle computer-controlled  $PI$  diffractometer with a graphite monochromator and a pulse-height analyzer was used throughout for preliminary experiments and for the collection of diffraction intensities. Molybdenum radiation ( $K\alpha_1$ ,  $\lambda = 0.70930 \text{ \AA}$ ;  $K\alpha_2$ ,  $\lambda = 0.71359 \text{ \AA}$ ) was used. The unit cell constant, as determined by a least-squares refinement of 15 intense reflections for which  $19^\circ < 2\theta < 24^\circ$ , is  $12.311(1) \text{ \AA}$ .

Data collection was done by methods described previously,<sup>12</sup> except that only one unique region of reciprocal space was examined at a scan rate ( $\omega$ ) of  $2^\circ \text{ min}^{-1}$  in  $2\theta$ . Standard deviations were assigned to individual reflections according to the formula.

$$\sigma(I) = \{\omega^2(CT + B_1 + B_2) + (PI)^2\}^{1/2}$$

where  $\omega$  is the scan rate,  $CT$  is the total integrated count,  $B_1$  and  $B_2$  are background counts, and the intensity  $I = \omega(CT - B_1 - B_2)$ . A value of 0.02<sup>13</sup> was assigned to the empirical parameter  $p$  to account for the reduced reliability of the more intense reflections. The intensities were corrected for Lorentz and polarization effects;<sup>14</sup> the contribution of the monochromator crystal was calculated assuming it to be half-perfect and half-mosaic in character. An absorption correction ( $\mu = 2.3 \text{ mm}^{-1}$ ) was judged to be negligible and was not applied.<sup>15</sup> All 891 reflections for which  $2\theta < 70^\circ$  were examined by counter methods. Of these, only the 266 for which  $I_o > 3\sigma(I_o)$  were used for structure solution and refinement.

## Structure Determination

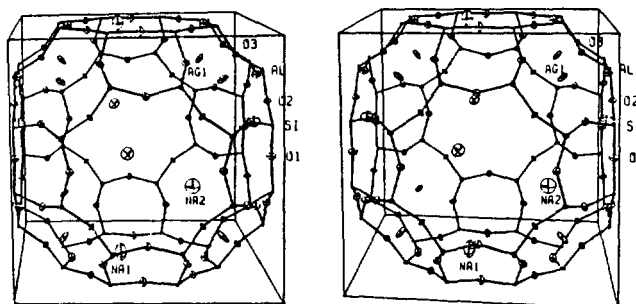
Full-matrix least-squares refinement was initiated using the atomic parameters of the framework atoms ((Si, Al), O(1), O(2), and O(3)), and of the cation positions at Ag(1) (6-ring) and Na(1) (8-ring) from the structures of  $Ag_{12}A$ <sup>1,2</sup> and  $Na_{12}A$ .<sup>16</sup> Anisotropic refinement of framework atoms and Ag(1) and isotropic refinement of Na(1) converged to the error indices.

$$R_1 = \sum |F_o - |F_c|| / \sum F_o = 0.13$$

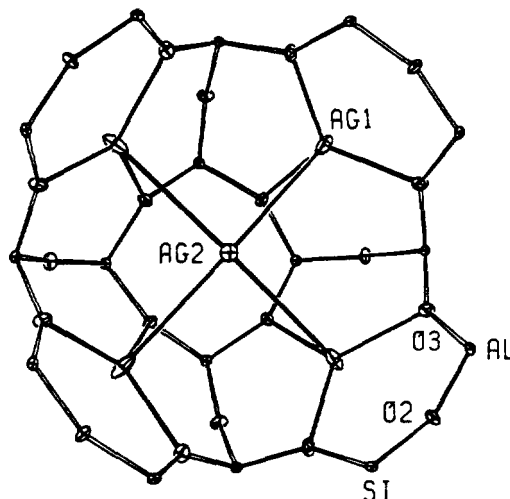
$$R_2 = \{\sum w(F_o - |F_c|)^2 / \sum wF_o^2\}^{1/2} = 0.14$$

A subsequent difference Fourier synthesis revealed a large peak  $11.6(6) \text{ e\AA}^{-3}$  in height at (0.0, 0.0, 0.17). This is the previously observed neutral silver atom position,<sup>1,2,17,18</sup> and was stable in least-squares refinement. Positional, occupancy, and anisotropic thermal parameter refinements of the framework and of the Ag(1), Na(1), and Ag(2) positions converged to the error indices,  $R_1 = 0.064$  and  $R_2 = 0.060$ .

The occupancies of these ions per unit cell refined to Ag(1) = 6.83(7), Na(1) = 2.8(3) and Ag(2) = 1.03(1). In zeolite A structures, 12 monovalent cations, or in this case 12 cations or Ag atoms, should be found per unit cell. Furthermore the 6-ring sites are usually favored, and all 8 6-ring sites are usually filled, more than the 6.83(7) found at Ag(1). When the thermal ellipsoid at Ag(1) became extremely elongated in subsequent refinement, and because the expected stoichiometry would now require that a  $Na^+$  ion be at a 6-ring site, the threefold-axis position was separated into Ag(1) and Na(2) and refined with the constraint that the sum of occupancies



**Figure 1.** A stereoview of a large cavity of dehydrated  $Ag_7Na_{12}A$  is shown using ellipsoids of 20% probability. The  $Ag^+$  and  $Na^+$  ions are distributed within their equipoints of partial occupancy in a plausible manner. This arrangement is seen in about 60% of the unit cells (ca 40% if  $Ag_6$  clusters coordinated to 8  $Ag^+$  ions have formed in 1/6 of the sodalite units. See reference 2 for a stereoview of  $Ag_6$  clusters). The remainder have 6 ions at Ag(1) and 2 at Na(2), not 7 and 1, respectively, as shown here.



**Figure 2.** The possible isolated Ag atom coordinated to 4  $Ag^+$  ions to give  $(Ag^+)_2$ , symmetry  $4mm$ . Each  $Ag^+$  ion coordinates to the 3 O(3) oxygens of a 6-ring.

Table 1. Positional, Thermal, and Occupancy Parameters

Atom	Wyckoff Position	x	y	z	$\beta_{11}$ or $\beta_{12}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	Occupancy Factor <sup>c</sup>
(Si,Al)	24(k)	0	1841(5)	3711(3)	20(4)	27(4)	14(4)	0	0	0(5)	24 <sup>d</sup>
O(1)	12(h)	0	2188(13)	5000	71(17)	41(15)	31(14)	0	0	0	12
O(2)	12(i)	0	2954(9)	2954(9)	44(14)	26(8)	26(8)	0	0	33(20)	12
O(3)	24(m)	1118(6)	1118(6)	3390(9)	29(6)	29(6)	47(10)	17(14)	10(10)	10(10)	24
Na(1)	12(i)	0	4314(31)	4314(31)	168(74)	105(39)	105(39)	0	0	-20(93)	3
Ag(1)	8(g)	1900(3)	1900(3)	1900(3)	65(3)	65(3)	65(3)	88(5)	88(5)	88(5)	6.6(1)
Ag(2)	6(e)	0	0	1715(16)	45(10)	45(10)	37(18)	0	0	0	1
Na(2)	8(g)	2296(104)	2296(104)	2296(104)	10(10) <sup>e</sup>						1.4(1)

<sup>a</sup>Positional and anisotropic thermal parameters are given  $\times 10^4$ . Numbers in parentheses are the esd's in units of least significant digit given for the corresponding parameter. The anisotropic temperature factor is  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$ . <sup>b</sup>Isotropic thermal parameters in units of  $\text{\AA}^2$ . <sup>c</sup>Occupancy factors are given as the number of atoms or ions per unit cell. <sup>d</sup>Occupancy for (Si) = 12 and occupancy for (Al) = 12.

Table 2. Selected Interatomic Distances ( $\text{\AA}$ ) and Angles (deg)<sup>a</sup>

(Si,Al)-O(1)	1.644(6)	Ag(1)-O(3)	2.283(9)
(Si,Al)-O(2)	1.656(5)	Ag(2)-O(3)	2.84(1)
(Si,Al)-O(3)	1.686(8)	Na(1)-O(1)	2.74(4)
		Na(1)-O(2)	2.37(4)
		Na(2)-O(3)	2.46(11)
		Ag(1)-Ag(2)	3.316(4)
		Ag(2)-Ag(2)'	2.99(2)
O(1)-(Si,Al)-O(2)	109.1(7)	Ag(1)-Ag(2)-Ag(1)'	89.7(6)
O(1)-(Si,Al)-O(3)	113.3(5)	Ag(1)-Ag(2)-Ag(1)''	172.1(6)
O(2)-(Si,Al)-O(3)	107.7(4)	O(3)-Ag(1)-O(3)'	119.9(4)
O(3)-(Si,Al)-O(3)'	109.4(6)	O(3)-Ag(2)-O(3)'	61.1(3)
(Si,Al)-O(1)-(Si,Al)'	149.8(11)	O(1)-Na(2)-O(3)	63(1)
(Si,Al)-O(2)-(Si,Al)	158.4(8)	O(3)-Na(2)-O(3)''	107(4)
(Si,Al)-O(3)-(Si,Al)'	143.8(7)		

<sup>a</sup>Numbers in parentheses are estimated standard deviations in the units of the least significant digit given for the corresponding value.

be 8.0. By this method, 6.6 Ag<sup>+</sup> ions at Ag(1) and 1.4 Na<sup>+</sup> ions at Na(2) were found at 6-ring sites. To allow the occupancies to sum to 12, that at Na(1) was fixed at 3, its maximum value, and that at Ag(2) at 1.

A final difference Fourier synthesis was featureless except for one small peak, 1.3(3) e $\text{\AA}^{-3}$  in height at (0.34, 0.5, 0.5), which was unstable in least-squares refinement.

The final refinement using anisotropic thermal parameters for all positions except Na(2), which was refined isotropically, converged at  $R_1 = R_2 = 0.064$ . The goodness-of-fit,  $[\sum_w(F_o - |F_c|)^2 / (m - s)]^{1/2}$ , is 2.69;  $m$  (266) is the number of observations, and  $s$  (34) is the number of variables in least-squares. All shifts in the final cycles of refinement were less than 20% of their corresponding esd's except that of the isotropic thermal parameter of Na(2) which shifted 36%.

The full-matrix least-squares program<sup>14</sup> used in all structure determinations minimized  $\sum_w(\Delta|F|)^2$ ; the weight ( $w$ ) of an observation was the reciprocal square of  $\sigma$ , its standard deviation. Atomic scattering factors for Ag<sup>+</sup>, Ag<sup>0</sup>, O<sup>-</sup>, Na<sup>+</sup>, and (Si, Al)<sup>2+</sup> were used.<sup>19,20</sup> The function describing (Si, Al)<sup>2+</sup> is the mean of the Si<sup>0</sup>, Si<sup>4+</sup>, Al<sup>0</sup>, and Al<sup>3+</sup> functions. All scattering factors were modified to account for the real component ( $f'$ ) of the anomalous dispersion correction.<sup>21,22</sup> Final positional,

Table 3. Deviations of Atoms ( $\text{\AA}$ ) from the (111) Plane at O(3)<sup>a</sup>

O(3)	0.20
Ag(1)	0.06
Na(2)	0.90
Ag(2)	-2.78

<sup>a</sup>A negative deviation indicates that the atom lies on the same side of the plane as the origin.

thermal, and occupancy parameters are presented in Table I; bond lengths and angles are given in Table II.

## Discussion

The 6.6 Ag<sup>+</sup> ions at Ag(1) are at the same position as was found in dehydrated Ag<sub>12</sub>-A.<sup>1,2</sup> Each Ag<sup>+</sup> ion lies on a threefold axis and is nearly at the center of a 6-ring (Table 3 and Figure 1). Each is trigonally coordinated at 2.28(1) $\text{\AA}$  to 3 O(3) framework oxygens. As compared to the sum of the Ag<sup>+</sup> and O<sup>2-</sup> radii, 2.58 $\text{\AA}$ ,<sup>23</sup> these bonds are quite short and therefore quite covalent.<sup>1,2</sup>

The 3 Na<sup>+</sup> ions at Na(1) are associated with 8-ring oxygens. These positions are located in the plane of the 8-rings, but not at their centers so that favorable approaches to framework oxygens may be made. Each Na(1) ion approaches 1 O(2) oxygen at 2.37 $\text{\AA}$  and 2 O(1) oxygens at 2.74 $\text{\AA}$ .

At Na(2), 1.4 Na<sup>+</sup> ions occupy a threefold-axis site near 6-rings and are recessed 0.9 $\text{\AA}$  into the large cavity from [111] plane at O(3) (Table 3). Each Na(2) ion is trigonally coordinated to 3 O(3) framework oxygens at 2.46 $\text{\AA}$ . For comparison, the sum of the conventional Na<sup>+</sup> and O<sup>2-</sup> radii is 2.29 $\text{\AA}$ .<sup>23</sup>

The fractional occupancies observed at Ag(1) and Na(2) indicate the existence of at least 2 types of unit cells with regard to the 6-rings. For example, 60% of the unit cells may have 7 Ag<sup>+</sup> ions at Ag(1) and 1 Na<sup>+</sup> ion at Na(2), and the remaining 40% would have 6 Ag<sup>+</sup> and 2 Na<sup>+</sup> at these positions, respectively. More extreme compositional variations are possible, but are considered less likely unless Ag<sub>6</sub> clusters have formed. Sodalite units with hexasilver clusters would be expected to have 8 Ag<sup>+</sup> ions at Ag(1), leaving other sodalite units to have 7 (ca 30%) or 6 (ca 70%) Ag<sup>+</sup> ions, complemented by 1 or 2 Na<sup>+</sup> ions, respectively, as above.

The Ag(2) position is very similar to that of the neutral silver atom in the structure of dehydrated partially decomposed  $Ag_{12}-A$ .<sup>1,2</sup> The distance between Ag(2) and the nearest oxygen at O(3) is quite long, 2.84(2)Å, as compared to the corresponding ion to ion distances observed, and about the same as was seen before between a neutral silver atom and framework oxygens.<sup>1,2</sup> The shortest available Ag(2)-Ag(2) distance, 2.98(2)Å, may be considered slightly longer than the Ag-Ag bond in silver metal, 2.89Å.<sup>24</sup> One may conclude that an average of 1 reduced silver atom per unit cell has been formed inside the sodalite unit, presumably by the reaction of a  $Ag^+$  ion, the twelfth ion, the ion in excess of the 11 of which can be accommodated at the 8 6-ring and 3 8-ring sites, with half of an oxygen atom (oxide ion) of the framework or of a residual water molecule. It may be that a neutral hex-silver cluster has formed in 1/6 of the sodalite units, or that an isolated atom exists in each sodalite unit, coordinated to at least 2 or 3  $Ag^+$  ions but probably the maximum number, 4, to give  $(Ag_6)^{+4}$ , symmetry  $4mm$ . This neutral silver atom was also seen in other structures such as  $Tl_{6.5}Ag_{5.5}-A$  dehydrated at 440°C,<sup>19</sup> and  $Ag_{12}-A$  treated first with  $H_2$  and then with  $O_2$ , both at 330°C.<sup>17</sup>

The cation which has been reduced is the  $Ag^+$  which is most easily reduced and the cation site which is no longer occupied is the least favorable one opposite a 4-ring in the large cavity. This position is the least satisfactory because the approach of the  $Ag^+$  ion to framework oxygens has been the longest (possibly virtual) and the most one-sided in previous studies.<sup>1,2,25</sup>

The ionic radius<sup>23</sup> of  $Ag^+$ , 1.26Å, is much larger than that of  $Na^+$ , 0.97Å. From a consideration of ionic radii only, one would expect the larger  $Ag^+$  ions to associate with the larger rings, the 8-rings. However,  $Ag^+$  ions are all found in 6-ring sites as predicted by the calculations of Nitta *et al.*<sup>9</sup> and demonstrated less directly by the experiments of Schöller *et al.*<sup>7</sup>

$Ag_{12}-A$  dehydrated at 350°C has 3 water molecules in each sodalite unit, together with 3  $Ag^+$  ions and no reduced silver atoms.<sup>25</sup>  $Ag_{12}-A$  dehydrated at temperatures  $\geq 400^\circ C$  for about 2 days has no residual water and contains reduced silver atoms.<sup>1,2</sup> In this work, we observe 370°C is a sufficiently high temperature to have brought about the complete dehydration and the partial reduction of  $Ag^+$  in  $Ag_{7.6}Na_{4.4}-A$ . Perhaps the formation of the silver atom and the loss of the last water molecule(s) occur together as a concerted process.

A comparison of this structure with that of dehydrated (at 350°C)  $Ag_6Na_6-A$  treated with  $H_2$ ,<sup>9</sup> and with dehydrated (at 350°C)  $Ag_{4.6}Na_{7.4}-A$  treated with  $H_2$ ,<sup>5</sup> indicates that all of the reduced silver atoms and 8-ring  $Ag^+$  ions in those structures were  $Ag^+$  ions in 6-rings before  $H_2$  was added, except for 1 silver atom per unit cell which may have formed during dehydration. Some 6-ring  $Ag^+$  ions moved to 8-ring sites to coordinate to silver atoms or clusters.

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