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## The Hexasilver Molecule Stabilized by Coordination to Six Silver Ions. The Structure of $(Ag^+)_6(Ag_6)$ . The Crystal Structure of an Ethylene Sorption Complex of Partially Decomposed Fully $Ag^+$ -Exchanged Zeolite A

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**Abstract:** The crystal structure of an ethylene sorption complex of partially decomposed fully  $Ag^+$ -exchanged zeolite A has been determined from three-dimensional x-ray diffraction data gathered by counter methods. The structure was solved and refined in the cubic space group  $Pm\bar{3}m$ ;  $a = 12.212(1) \text{ \AA}$  at  $23(1)^\circ\text{C}$ . The complex was prepared by dehydration and partial decomposition at  $400^\circ\text{C}$  and  $5 \times 10^{-6}$  Torr for 4 days, followed by exposure to 120 Torr of ethylene gas at  $23^\circ\text{C}$ . Two types of unit cells can be distinguished. About 46% contain, in the sodalite unit, the octahedral molecule  $Ag_6$  complexed to six  $Ag^+$  cations at 6-ring sites to give  $(Ag^+)_6(Ag_6)$ . The Ag-Ag bond length,  $2.850(4) \text{ \AA}$ , is notably less than the  $2.928(4) \text{ \AA}$  distance found in  $(Ag^+)_8(Ag_6)$ , presumably because fewer cations can draw bonding electron density from the  $Ag_6$  molecule. The Ag- $Ag^+$  coordination approach is  $3.26(2) \text{ \AA}$ , less than the distance of  $3.33(1) \text{ \AA}$  in  $(Ag^+)_8(Ag_6)$ , presumably because the  $Ag^+$ -Ag interaction is correspondingly stronger. The remaining 54% of the unit cells have the following arrangement: one 6-ring  $Ag^+$  ion is in the sodalite unit, and seven others are recessed approximately  $1.2 \text{ \AA}$  into the large zeolite cavity where each forms a lateral  $\pi$  complex with an ethylene molecule. These latter  $Ag^+$  ions are in a near tetrahedral environment,  $2.49(1) \text{ \AA}$  from three framework oxide ions and  $2.54(8) \text{ \AA}$  from each carbon atom of an ethylene molecule (which is here counted as a monodentate ligand.) Approximately two additional  $Ag^+$  cations are associated with 8-oxygen rings in all unit cells. Full-matrix least-squares refinement converged to a weighted  $R_2$  index (on  $F$ ) of 0.071 using the 408 independent reflections for which  $I > 3\sigma(I)$ .

### Introduction

Vacuum-dehydrated fully  $Ag^+$ -exchanged zeolite A probably contains uncharged octahedral silver clusters,  $Ag_6$ , at the centers of most of its sodalite cavities.<sup>1,2</sup> (With far less likelihood, the clusters could be  $Ag_5$  or  $Ag_4$ , whose structures would be octahedra with one or any two vertices, respectively, missing.<sup>1</sup>) These six-atom molecules are closest packed, are the smallest possible fully developed single crystals of silver, and have the natural growth form [111] of silver metal. The number of silver clusters has been observed to increase with dehydration time and temperature until approximately two-thirds of the sodalite units contain silver clusters; the remaining one-third do not. To date, attempts to carry this reaction further have led to the migration of silver atoms out of the zeolite structure, to form crystallites of metallic silver on the surface of the zeolite crystal.<sup>3</sup>

Ammonia gas at  $25^\circ\text{C}$  can also displace the  $Ag_6$  molecules from the zeolite structure. Crystallographic studies<sup>4</sup> have shown that under certain conditions, sorbed ammonia has trimerized and complexed with  $Ag^+$  ions to form the saturated hydronitrogen complexes  $Ag_2(N_3H_5)_3^{2+}$  and  $Ag(N_3H_3)^+$  within the zeolite, displacing  $Ag_6$  as ligands to  $Ag^+$ . At tem-

peratures between  $23$  and  $75^\circ\text{C}$ ,  $N_3H_3$  (cyclo-triazane) and  $N_3H_5$  (triazane) have been identified mass spectrometrically in the gas phase above the zeolite.<sup>4</sup>

As a continuation of the study of the unusual chemistry of silver ions, silver clusters, and molecules within this zeolite, an ethylene sorption complex of fully dehydrated  $Ag_{12}$ -A<sup>5</sup> was prepared and its crystal structure determined.

Carter et al.<sup>6</sup> have studied the sorption of ethylene at room temperature onto a series of ion-exchanged synthetic near-faujasites by infrared spectroscopy and by microcalorimetry. They found that  $C_2H_4$  molecules form laterally held  $\pi$  complexes of symmetry  $C_2$ . Of the transition metal ions examined,  $Ag^+$  and  $Cd^{2+}$  were found to hold  $C_2H_4$  most strongly. Furthermore, the adsorbed ethylene molecule is reported to be freely rotating in all cases, except in its  $Ag^+$  complex.

In the crystal structure of an ethylene sorption complex<sup>7</sup> of partially Co(II)-exchanged zeolite A,  $Co_4Na_4$ -A, the four Co(II) ions are found at 6-ring<sup>2</sup> sites. Each Co(II) is recessed  $0.58 \text{ \AA}$  into the large cavity where it complexes laterally to an ethylene molecule. The relatively long ( $2.51(6) \text{ \AA}$ ) and weak Co(II)- $C_2H_4$  interaction is ascribed largely to the polarization of the  $\pi$  electron density of ethylene by the highly charged Co(II) ion.

**Table I.** Positional, Thermal,<sup>a</sup> and Occupancy Parameters for the Ethylene Sorption Complex of Ag<sub>12</sub>-A

	Wyckoff position	x	y	z	$\beta_{11}^b$ or $B_{iso}$						Occupancy factor	
					$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	Varied <sup>c</sup>	Fixed	
(Si,Al)	24(k)	0	1820 (3)	3678 (3)	27 (3)	25 (3)	20 (2)	0	0	5(4)	1 <sup>d</sup>	1 <sup>d</sup>
O(1)	12(h)	0	2007 (10)	1/2	39 (10)	54 (11)	22 (8)	0	0	0	1	1
O(2)	12(i)	0	3009 (6)	3009 (6)	53 (10)	15 (5)	15 (5)	0	0	23 (12)	1	1
O(3)	24(m)	1096 (5)	1096 (5)	3278 (7)	56 (5)	56 (5)	54 (8)	18 (13)	15 (9)	15 (9)	1	1
Ag(1)	8(g)	1341 (33)	1341 (33)	1341 (33)	33 (19)	33 (19)	33 (19)	39 (35)	39 (35)	39 (35)	0.077 (31)	0.068
Ag(2)	8(g)	1879 (19)	1879 (19)	1879 (19)	135 (64)	135 (64)	135 (64)	227 (128)	227 (128)	227 (128)	0.323 (62)	0.345
Ag(3)	8(g)	2401 (5)	2401 (5)	2401 (5)	38 (2)	38 (2)	38 (2)	11 (6)	11 (6)	11 (6)	0.472 (32)	0.473
Ag(4)	6(e)	0	0	1650 (3)	26 (2)	26 (2)	6 (2)	0	0	0	0.433 (7)	0.460
Ag(5)	24(l)	287 (28)	4074 (43)	1/2	4.5 (1.6) <sup>e</sup>						0.040 (7)	0.045
Ag(6)	12(i)	0	4384 (24)	4384 (24)	4.7 (1.5) <sup>e</sup>						0.059 (14)	0.090
C	48(n)	2818 (67)	3507 (71)	4116 (72)	9.5 (3.9) <sup>e</sup>						0.157 (11) <sup>f</sup>	0.152

<sup>a</sup> Positional and anisotropic parameters are given  $\times 10^4$ . Numbers in parentheses are the estimated standard deviations in the units of the least significant figure 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> Root mean square displacements can be calculated from  $\beta_{ii}$  values using the formula  $\mu_i = 0.225a(\beta_{ii})^{1/2}$ , where  $a = 12.212 \text{ \AA}$ . <sup>c</sup> All positional and thermal parameters in this table were calculated as the occupancy parameters varied freely. <sup>d</sup> Occupancy for (Si) = 1/2; occupancy for (Al) = 1/2. <sup>e</sup> Isotropic thermal parameter in units of  $\text{\AA}^2$ . <sup>f</sup> This value was constrained to be no more than one-third the occupancy of Ag(3), corresponding to one ethylene molecule per silver ion at that position.

## Experimental Section

Crystals of zeolite 4A were prepared by Charnell's method,<sup>9</sup> modified by the inclusion of seed crystals from a previous preparation. A single crystal 0.08 mm on an edge was selected and lodged in a fine capillary.  $\text{AgNO}_3$  (0.05M) was allowed to flow past the crystal at about 1.5 cm/s for 6 days; since the exchange of  $\text{Ag}^+$  for  $\text{Na}^+$  has been shown to be facile and complete after much milder treatment,<sup>8</sup> complete exchange was assured in this case. The clear, colorless, hydrated  $\text{Ag}^+$ -exchanged crystal was dehydrated (and partly decomposed) for 4 days at 400 °C and  $5 \times 10^{-6}$  Torr. The crystal initially became black, but this color lightened to brick red and ultimately to clear yellow during the dehydration treatment. At this point, the crystal was treated with 120 Torr of zeolitically dried ethylene for 1 h at 23 °C. The resulting drab green crystal, still in its ethylene atmosphere, was sealed in its capillary by torch.

**X-Ray Data Collection.** The cubic space group  $Pm\bar{3}m$  (no systematic absences) appeared to be appropriate.<sup>7,10-12</sup> A Syntex four-circle computer-controlled diffractometer with molybdenum radiation ( $K\alpha_1$ ,  $\lambda = 0.70930 \text{ \AA}$ ;  $K\alpha_2$ ,  $\lambda = 0.71359 \text{ \AA}$ ), a graphite monochromator, and a pulse-height analyzer was used throughout for preliminary experiments and for the collection of diffraction intensities. The unit cell constant, as determined by a least-squares refinement of 15 intense reflections for which  $20^\circ < 2\theta < 24^\circ$ , is 12.212 (1)  $\text{\AA}$  at 23 °C.

Reflections from two intensity-equivalent regions of reciprocal space ( $hkl$ ,  $h \leq k \leq l$ ; and  $h\bar{l}k$ ,  $h \leq l \leq k$ ) were examined using the  $\theta$ - $2\theta$  scan technique. Each reflection was scanned at a constant rate of 1.0  $\text{deg min}^{-1}$  from  $0.8^\circ$  (in  $2\theta$ ) below the calculated  $K\alpha_1$  peak to  $0.8^\circ$  above the  $K\alpha_2$  maximum. Background intensity was counted at each end of the scan range for a time equal to half the scan time. The intensities of three reflections in diverse regions of reciprocal space were recorded after every 100 reflections 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. Although few reflections were significantly greater than background for high  $2\theta$  values, this limit was selected to allow the data set to be more complete.

The raw data from each region were corrected for Lorentz and polarization effects, including that due to incident beam monochromatization; the reduced intensities were merged; and the resultant estimated standard deviations were assigned to each averaged reflection by the computer program COMPARE.<sup>13</sup> The mean intensity for a reflection was calculated as  $I = (I_{hkl} + I_{h\bar{l}k})/2$ , where  $I_{hkl} = [CT - B_1 - B_2]/(\omega)$ , CT is the total integrated count,  $B_1$  and  $B_2$  are the background counts, and  $\omega$  is the scan rate. The standard deviation of  $I$  was calculated using

$$\sigma(I) = (\sigma^2(I_{hkl}) + \sigma^2(I_{h\bar{l}k}))^{1/2}/2$$

and the standard deviation of each unmerged reflection is

$$\sigma(I_{hkl}) = [((CT + B_1 + B_2)\omega^2) + (pI_{hkl})^2]^{1/2}$$

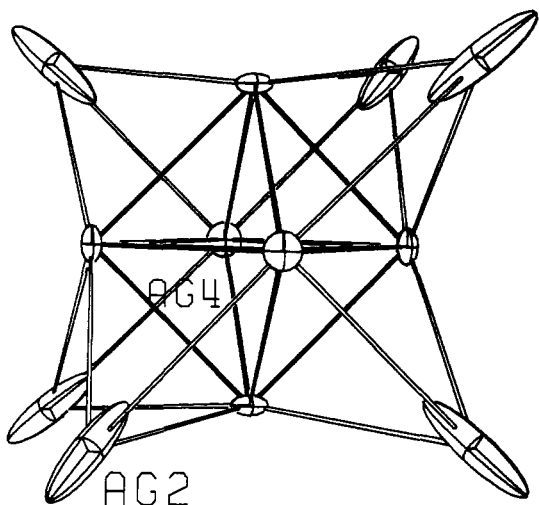
The value of  $p$  was taken as 0.02,<sup>14</sup> a value found to be appropriate for the instrumentation used. No absorption correction was applied to the data;  $\mu = 34.8 \text{ cm}^{-1}$  and transmission coefficients were expected to range from 0.750 to 0.780. Of the 870 pairs of reflections examined, only the 408 whose net counts exceeded three times their corresponding esd's were used in structure solution and refinement.

**Structure Determination.** Full-matrix least-squares refinement of the ethylene complex of  $\text{Ag}_{12}$ -A was initiated using the atomic parameters of the framework atoms ((Si,Al), O(1), O(2), and O(3)) in dehydrated  $\text{Ag}_{12}$ -A.<sup>1</sup> Anisotropic refinement of the framework atoms converged to an  $R_1$  index,  $(\sum |F_o - |F_c||)/\sum F_o$ , of 0.51 and a weighted  $R_2$  index,  $(\sum w(F_o - |F_c|)^2/\sum wF_o^2)^{1/2}$ , of 0.57. A subsequent difference Fourier function served to reveal the positions of the  $\text{Ag}^+$  ions at Ag(1), Ag(2), Ag(3), and Ag(4) (see Table I). Anisotropic refinement including these  $\text{Ag}^+$  ions converged to  $R_1 = 0.21$  and  $R_2 = 0.24$ . Successive difference Fourier syntheses indicated two more  $\text{Ag}^+$  positions at Ag(5) and Ag(6). The carbon atoms of the ethylene molecules appeared at the 24-fold position (0.27, 0.38, 0.38) with a peak height of  $2.0 \text{ e \AA}^{-3}$ ; this corresponds closely to the final result, that approximately 7.56 carbon atoms are located very near this position.

It was assumed that one  $\text{C}_2\text{H}_4$  molecule is associated with each Ag(3) ion, such coordination being the reason that Ag(3) is recessed approximately 1.2  $\text{\AA}$  into the large cavity at a near-tetrahedral 4-coordinate position. Refinement of about eight carbon atoms per unit cell at this position, constrained to be no more than twice the number of  $\text{Ag}^+$  ions at Ag(3), converged readily, but gave a long C=C bond length (1.9  $\text{\AA}$ ) and a large isotropic thermal parameter (19  $\text{\AA}^2$ ). A trial refinement with carbon at a general position ( $x, y, z$ ; atom C in Table I), like that in the ethylene sorption complex of  $\text{Co}_4\text{Na}_4$ -A,<sup>7</sup> resulted in an opportunity to select a more satisfactory C=C bond length (1.19  $\text{\AA}$ ) and provided a lower isotropic thermal parameter (9.5  $\text{\AA}^2$ ) for carbon.

The structure model which has emerged cannot be reasonably interpreted by statistically distributing the atoms and ions within their equipoints to give a single representative unit cell. An interpretation consistent with the structure of a dehydrated  $\text{Ag}_{12}$ -A<sup>1</sup> indicates that this one is a mixture of two differently occupied unit cells whose average is the crystallographic result.

Some discussion of the structure prior to the sorption of ethylene is required at this point. A molecule of  $\text{Ag}_6$  (probably) is found in the sodalite unit of dehydrated  $\text{Ag}_{12}$ -A.<sup>1</sup> This molecule lies at the center of a cube of eight 6-ring  $\text{Ag}^+$  ions toward which it acts as a ligand. After the absorption of ethylene, the freely varied occupancies of all silver positions indicate that the occupancy at Ag(2) is almost identical with that at Ag(4), and that the occupancy at Ag(3) is very nearly seven times that at Ag(1). These numbers indicate that there are two kinds of unit cells. One kind has six Ag(4) atoms inside the sodalite unit and six Ag(2) ions, to give the complex  $(\text{Ag}^+)_6(\text{Ag}_6)$ , Figure 1, somewhat different from that found in dehydrated  $\text{Ag}_{12}$ -A,<sup>1</sup>  $(\text{Ag}^+)_8(\text{Ag}_6)$ . Additional  $\text{Ag}^+$  ions per unit cell, at Ag(5) and Ag(6), are associated with the 8-rings. The other unit cell contains one Ag(1) ion



**Figure 1.**  $(Ag^+)_6(Ag_6)$ . The octahedral hexasilver molecule at Ag(4) positions stabilized by complexation to six silver ions at Ag(2) positions. The symmetry of the complex as shown is  $(\bar{3})(2/m)(D_{3d})$ ; the point symmetry of the  $Ag_6$  molecule within is  $(4/m)(\bar{3})(2/m)$ . Ellipsoids of 50% probability are used.

inside the sodalite unit and seven at Ag(3), complexed to seven ethylene molecules in the large cage, as is shown in Figure 2. This second kind of unit cell would also contain ions at the positions Ag(5) and Ag(6). Although slightly more than two  $Ag^+$  ions appear at Ag(5) and Ag(6) in the average unit cell, these are likely to be distributed unevenly among the two kinds of unit cells, in part to balance local charges better.

By varying the fraction of unit cell structures of each kind so that the sum remains 1.0, a rather sharp minimum, as indicated by the  $R$  indices based on  $F$  calculations (an intimate mixing of the two kinds of unit cells is assumed), has been found. It is estimated, to within 1%, that 46% of the unit cells are of the first kind (containing  $Ag_6$  complexed to  $Ag^+$  ions), and 54% are of the second kind (containing ethylene molecules complexed to  $Ag^+$ ). The occupancy values labeled "fixed" in Table I are the result of this procedure. At convergence,  $R_1 = 0.088$  and  $R_2 = 0.078$ .

In comparison, least-squares refinement of a model with all occupancies independently variable except those of the zeolite framework, and all thermal parameters refined anisotropically except those of Ag(5), Ag(6), and C, converged at  $R_1 = 0.087$  and  $R_2 = 0.071$ . The positional, thermal, and varied occupancy parameters from this refinement are given in Table I. The goodness-of-fit for the latter (unconstrained) refinement is  $(\sum w(F_o - |F_c|)^2 / (m - s))^{1/2} = 3.58$ , where  $m$  (408) is the number of observations and  $s$  (48) is the number of variables in least-squares refinement. A final difference Fourier function, whose estimated standard deviation was  $0.15 \text{ e } \text{\AA}^{-3}$ , showed

**Table II.** Selected Interatomic Distances ( $\text{\AA}$ ) and Angles (deg)

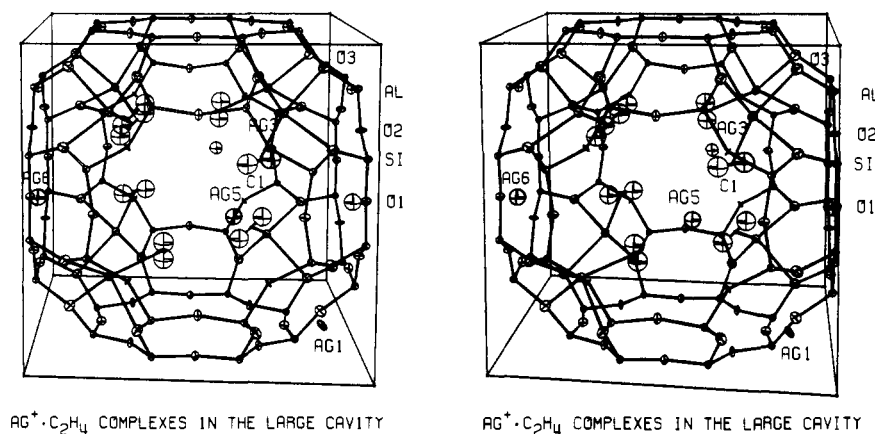
(Si,Al)-O(1)	1.630 (3)
(Si,Al)-O(2)	1.667 (8)
(Si,Al)-O(3)	1.676 (7)
Ag(1)-O(3)	2.403 (7)
Ag(2)-O(3)	2.179 (25)
Ag(3)-O(3)	2.494 (9)
Ag(4)-O(3)	2.745 (9)
Ag(5)-O(1)	2.548 (52)
Ag(6)-O(2)	2.373 (30)
Ag(3)-C	2.54 (8)
C-C	1.19 (12)
Ag(4)-Ag(4)	2.850 (4)
Ag(2)-Ag(4)	3.258 (24)
O(1)-(Si,Al)-O(2)	111.2 (5)
O(1)-(Si,Al)-O(3)	111.3 (5)
O(2)-(Si,Al)-O(3)	108.5 (4)
O(3)-(Si,Al)-O(3)	105.9 (6)
(Si,Al)-O(1)-(Si,Al)	163.8 (4)
(Si,Al)-O(2)-(Si,Al)	148.6 (6)
(Si,Al)-O(3)-(Si,Al)	139.3 (6)
O(3)-Ag(1)-O(3)	103.3 (16)
O(3)-Ag(2)-O(3)	119.7 (12)
O(3)-Ag(3)-O(3)	98.1 (4)
O(3)-Ag(4)-O(3)	58.3 (3)
Ag(2)-Ag(4)-Ag(2)	89.6 (8)
Ag(3)-C-C	77 (6)
C-Ag(3)-C	27 (4)
O(3)-Ag(3)-C	96 (2)

two peaks, at  $(0.0, 0.19, 0.38; 1.5 \text{ e } \text{\AA}^{-3})$  and  $(0.25, 0.25, 0.25; 1.9 \text{ e } \text{\AA}^{-3})$ . The first is too close to the (Si,Al) position, and the second is too close to Ag(3).

The quantity minimized in the least-squares treatment was  $\sum w(F_o - |F_c|)^2$ , where the weights ( $w$ ) are the reciprocal squares of  $\sigma(F_o)$ , the standard deviation of each observation. Atomic scattering factors<sup>15,16</sup> for  $Ag^+$ ,  $O^-$ , C (valence), and (Si,Al)<sup>1.75+</sup> were used. The function describing (Si,Al)<sup>1.75+</sup> is the mean of the  $Si^0$ ,  $Si^{4+}$ ,  $Al^0$ , and  $Al^{3+}$  functions. All scattering factors were modified to account for the real component ( $\Delta f'$ ) of the anomalous dispersion correction.<sup>17</sup> Bond lengths and selected angles are given in Table II.

## Discussion

When fully  $Ag^+$ -exchanged zeolite A is dehydrated, the eight threefold-axis  $Ag^+$  cations move to the centers of the 6-rings to sites of three coordination.<sup>1,3</sup> The remaining four  $Ag^+$  ions might have been expected at sites like those found for the corresponding cations in the dehydrated structures of  $K_{12}\text{-A}$ ,  $Rb_{11}\text{-Na-A}$ ,  $Cs_7K_5\text{-A}$ , and  $Tl_{12}\text{-A}$ .<sup>18</sup> Three would be associated with 8-rings, and the remaining one would be at a



**Figure 2.** A stereoview of the large cavity showing the ions at Ag(5) and Ag(6). About 54% of the sodalite units are surrounded by this many (seven)  $C_2H_4$  complexes. This is the maximum number of molecules of  $C_2H_4$  which might appear in any one large cavity, although fewer, three or four, are more likely. The hydrogen atoms, whose positions were not determined, are not shown. Ellipsoids of 20% probability are used.

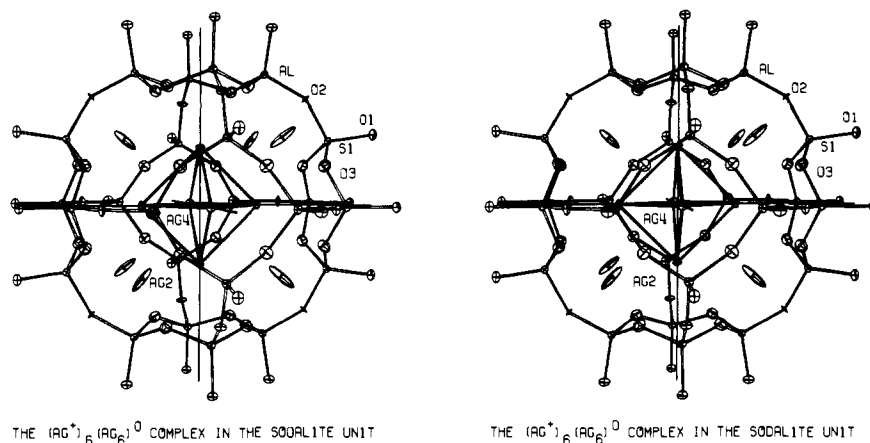


Figure 3. A stereoview of a sodalite unit containing an octahedral  $\text{Ag}_6$  molecule complexed to six  $\text{Ag}^+$  ions is shown. Ellipsoids of 20% probability are used.

site of zero,<sup>18a,b,c,e</sup> or more likely near zero,<sup>18d</sup> coordination.

What is actually observed,<sup>1</sup> in six separate crystallographic determinations,<sup>3</sup> is the progressive decomposition of the  $\text{Ag}_2\text{O}$  component of the structure (if the unit cell formula is written as  $6\text{Al}_2\text{O}_3 \cdot 12\text{SiO}_2 \cdot 6\text{Ag}_2\text{O}$ ) to form the elements,  $\text{Ag}^0$  and  $\text{O}_2$ . As before,<sup>1,3</sup> a significant decrease in the occupancy of one or more of the oxide positions, which must occur as  $\text{O}_2$  is produced, was not found, presumably because only 1.4 of the 48 oxide ions per unit cell is involved, and the diffraction data are not sensitive enough to reveal such detail. However, the evolution of  $\text{O}_2$  has been observed.<sup>19</sup>

The  $\text{Ag}^+$  ions are reduced in order; the least suitably coordinated ions react first. In all cases, the proposed zero or near zero coordinate ion is not observed—it has already been reduced. Upon heating for 1–10 days at 375 to 450 °C, a progressive reduction of the 8-ring  $\text{Ag}^+$  ions with time is observed; the 6-ring ions do not react. At 475 °C, the reduction of  $\text{Ag}^+$  ions at all sites proceeds rapidly enough to approach completion in 1–2 weeks. The heating time and temperature treatment for the crystal whose structure is reported here was such that approximately 2.76  $\text{Ag}^0$  atoms have formed per unit cell, corresponding to the reduction of the zero or near zero coordinate  $\text{Ag}^+$  ion and approximately 1.76 of the 3.0 8-ring  $\text{Ag}^+$  cations. If the assumption<sup>1</sup> leading to the conclusion that neutral  $\text{Ag}_6$  molecules (and not  $\text{Ag}_4$  or  $\text{Ag}_5$ ) form in zeolite A is correct, then 46% of the unit cells in this crystal initially contained  $\text{Ag}_6$  in their sodalite units before ethylene was sorbed.

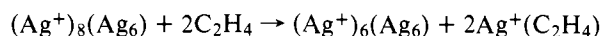
This structure provides some confirmatory evidence that the silver clusters involve six silver atoms, and not five or four (arranged at the vertices of an octahedron with one or any two positions vacant) as remained possible according to the evidence presented in a previous report.<sup>1</sup> The formula of the  $\text{Ag}_n$  complex is  $(\text{Ag}^+)_n(\text{Ag}_n)$  where  $n = 6, 5,$  or  $4$ . It appears chemically unreasonable that the stoichiometry  $(\text{Ag}^+)_5(\text{Ag}_5)$  would be the stable one at this site whose symmetry is  $(4/m)(\bar{3})(2/m)(O_h)$ , considering the further requirement that  $\text{Ag}^+$  is at  $\text{Ag}(2)$  and  $\text{Ag}^0$  is at  $\text{Ag}(4)$ . If  $(\text{Ag}^+)_4(\text{Ag}_4)$  were correct, a substantially larger  $\text{Ag}^0$  thermal parameter or a deviation of the  $\text{Ag}^0$  atoms from their fourfold axis position would be expected for  $\text{Ag}^+$  ions arranged at the vertices of an irregular tetrahedron, a rectangle, or a square. The possibility that a square of four silver atoms exists centered within a regular tetrahedron of four silver ions remains to be considered.

Several inconclusive but appealing arguments can be presented which disfavor the  $\text{Ag}_4$  square within a  $4\text{Ag}^+$  regular tetrahedron. Some have been presented earlier.<sup>1</sup> If the square were to exist, the sites above and below it, to complete a closest packed arrangement as in the structure of bulk silver and of

many other metals, should appear very attractive to two additional atoms which could bind to the already existing silver atoms and  $\text{Ag}^+$  ions. That the binding energy per atom increases as metal clusters increase in size has been shown by quantum mechanical calculations, on small lithium clusters,<sup>20</sup> for example. In line with this result, it can readily be seen that each silver atom in  $\text{Ag}_6$  can bond to four others, but a silver atom in square  $\text{Ag}_4$  can bond to only two. It is a common experimental observation that very small metal particles cluster to form larger ones; a reason for this clustering to stop at a two-thirds filling of the  $\text{Ag}(4)$  position appears to be lacking. This position is filled when the cluster size reaches six.

As a final argument, it has been noted that the threefold axis is relatively robust in zeolite A. It tends to endure when a plausible placement of atoms or ions in any particular unit cell requires a lowering of the overall symmetry. In  $\text{Ca}_4\text{Na}_4\text{A} \cdot 5.65\text{H}_2\text{O}$ ,  $\bar{3}(S_6)$  symmetry is preserved. This is a subset of that proposed for  $(\text{Ag}^+)_6(\text{Ag}_6)$ ,  $\bar{3}(2/m)(D_{3d})$ . In all of the structures which show zero coordinate cations<sup>18a-c,e</sup> only a threefold axis persists, and the same is true for a series of other zeolite A structures determined in this laboratory.<sup>2c</sup> The  $\text{Ag}_4$  square within a four  $\text{Ag}^+$  regular tetrahedron, at positions  $\text{Ag}(4)$  and  $\text{Ag}(2)$ , respectively, has symmetry  $\bar{4}2m(D_{2d})$  which does not contain a threefold axis. For this reason also, the  $\text{Ag}_4$  molecule is considered less likely.

The sorption of ethylene has little effect on the  $\text{Ag}_6$  clusters; their numbers are unaltered and their atomic coordinates are only slightly changed. Ethylene acts as a titrating agent which forms a lateral  $\pi$  complex (see Figure 4) with 6-ring  $\text{Ag}^+$  ions, two of which had previously been complexed to the ligand molecule  $\text{Ag}_6$  (see Figures 1 and 3). The formula of the  $\text{Ag}_6$  complex which exists in 46% of the sodalite units is therefore  $(\text{Ag}^+)_6(\text{Ag}_6)$ . This indicates, in comparison to previous results,<sup>1</sup> that the reaction



has occurred in the zeolite environment. For this reaction, the zeolite framework has acted as a solvent by completing the coordination spheres of all of the  $\text{Ag}^+$  ions in the above net reaction with three  $\text{O}(3)$  oxide ions.

As the hexasilver molecule changes its coordination number from eight  $\text{Ag}^+$  ions to six  $\text{Ag}^+$  ions, its  $\text{Ag}-\text{Ag}$  bond length (the edge length of the octahedron) decreases from 2.928 (4) Å to 2.850 (4) Å. This change is consistent with the diminished ability of the six  $\text{Ag}^+$  ions to draw bonding electron density from the hexasilver molecule by coordination. (Accordingly, the  $\text{Ag}-\text{Ag}$  bond in  $(\text{Ag}^+)_n(\text{Ag}_6)^0$ ,  $6 > n \geq 0$ , should be less than 2.85 Å; therefore, in an uncomplexed  $\text{Ag}_6$  cluster, the  $\text{Ag}-\text{Ag}$  bond should be less than that in bulk silver metal.)

**Table III.** Deviation (Å) of Atoms from the (111) Plane at O(3)<sup>a</sup>

	C <sub>2</sub> H <sub>4</sub> complex	Dehydrated Ag <sub>12</sub> -A (3.5 Ag <sup>0</sup> ) <sup>b</sup>
O(2)	0.39	0.26
Ag(1)	-1.02	
Ag(2)	0.11	0.13
Ag(3)	1.22	
Ag(4)	-2.69	-2.73
C	3.50	

<sup>a</sup> A negative deviation indicates that the atom lies on the same side of the plane as the origin. <sup>b</sup> Reference 1.

Supporting this scheme, the Ag<sup>+</sup>-Ag interaction, 3.26 (2) Å, is somewhat less than the corresponding 3.33 (1) Å approach in (Ag<sup>+</sup>)<sub>8</sub>(Ag<sub>6</sub>) because the more electron-rich Ag<sub>6</sub> molecule can be a better base to the six Ag<sup>+</sup> ions to which it is a ligand.

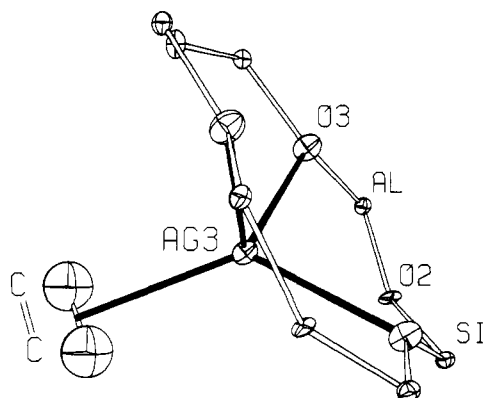
To coordinate to ethylene, the ions at Ag(3) have moved significant distances (ca. 1.1 Å) further into the large cage (see Figures 2 and 4) and away from their triads of three O(3) oxide ions, to more tetrahedral coordination situations (considering ethylene to be monodentate). The lengths of the Ag(3)-O(3) bonds have increased from 2.25 Å in dehydrated Ag<sub>12</sub>-A<sup>1</sup> to 2.49 (1) Å in this structure as the coordination of Ag<sup>+</sup> has changed from trigonal to near tetrahedral, an increase of one in coordination number. This Ag(3)-O(3) bond is approximately the same length as that (2.46 (2) Å) in the triazane and cyclotriazane (N<sub>3</sub>H<sub>5</sub> and N<sub>3</sub>H<sub>3</sub>) complex<sup>4</sup> of dehydrated Ag<sub>12</sub>-A, prepared by the sorption of ammonia. The O(3)-Ag(3)-O(3) angle has decreased accordingly from a nearly planar value, 119.6 (4)°, in dehydrated Ag<sub>12</sub>-A to 98.1 (4)° after ethylene complexation.

The 54% of the sodalite units which do not contain Ag<sup>+</sup>-complexed Ag<sub>6</sub> molecules hold instead a single Ag<sup>+</sup> ion at Ag(1). This is in accord with the frequent result<sup>2c</sup> that, as some ions are drawn into the large cavity, to form complexes or because their size keeps them from lying in the 6-ring plane, others move into the small cavity for similar reasons or as though to preserve a charge balance with respect to the spherical surface of the sodalite unit. An ethylene molecule could not be found in the sodalite unit (probably because the experimental data are insufficiently sensitive) where it might complex to the ion at Ag(1) which has receded to a position about 1.0 Å into the sodalite cage from the 6-ring plane at O(3) (Table III).

Those 54% of the sodalite units which do not contain Ag<sub>6</sub> molecules are surrounded by seven molecules of C<sub>2</sub>H<sub>4</sub> in the large cavities, complexed to seven Ag<sup>+</sup> ions at Ag(3). See Figure 2. The two carbon atoms of the ethylene molecule are equivalent in the complex, each 2.54 (8) Å from Ag(3), although the threefold axis on which the ions at Ag(3) lie does not intersect the C=C bond, as can be seen in Figure 4.

Because of the combined effects of disorder (the averaging of the Al and Si positions into a single (Si,Al) position, of the oxide ion positions as though the coordination spheres of Si and Al were the same size, and of the two kinds of unit cells) and moderately high thermal motion, the ethylenic double bond length (1.19 (12) Å) is foreshortened and inaccurately determined. It is nearly the same as that found in the ethylene sorption complex of Co<sub>4</sub>Na<sub>4</sub>-A,<sup>7</sup> 1.21 (11) Å. In neither determination is the deviation from the 1.334 Å bond length in ethylene gas<sup>22</sup> significant.

The bonding between the silver ion at Ag(2) and ethylene can be described in terms of two components according to the Chatt-Dewar model.<sup>23</sup> A  $\sigma$  component arises from the overlap of a filled ethylene  $\pi$  orbital and a vacant Ag<sup>+</sup> 5s orbital, and a  $\pi$  component occurs by the overlap of the filled 4d orbitals of Ag<sup>+</sup> with the vacant antibonding  $\pi^*$  orbital of ethylene. By



**Figure 4.** A  $Ag(C_2H_4)^+$  complex in the large cavity. The approximately tetrahedral coordination about Ag<sup>+</sup> can be seen. The hydrogen atoms, whose positions were not determined, are not shown. Ellipsoids of 20% probability are used.

the latter interaction, the C=C bond order may be diminished by back-donation.

Carter et al.<sup>6</sup> studied the sorption of ethylene by a series of transition metal ion exchanged zeolite X samples using calorimetric and IR methods. They found that ethylene is relatively weakly held and that it can readily be removed by evacuation at room temperature, unless the ion involved is Ag<sup>+</sup> or Cd<sup>2+</sup>. The Ag(3)-C bond length herein reported, 2.54 (8) Å, indicates that the ethylene is moderately firmly held by the Ag<sup>+</sup> ion at Ag(3). This bond length can be compared with distances of 2.48–2.51 Å in acenaphthene AgClO<sub>4</sub>,<sup>24</sup> 2.50–2.63 Å in benzene AgClO<sub>4</sub>,<sup>25</sup> 2.45–2.56 Å in anthracene [AgClO<sub>4</sub>]<sub>4</sub>·4H<sub>2</sub>O,<sup>25</sup> 2.60–2.63 Å<sup>24</sup> in naphthalene [AgClO<sub>4</sub>]<sub>4</sub>·4H<sub>2</sub>O,<sup>25</sup> and 2.47–2.92 Å in benzene AgAlCl<sub>4</sub>.<sup>26</sup>

Although the uncertainties in the carbon position are large and the determination of the C=C distance is poor, it is still clear that the ethylene molecules make no significant approaches to the zeolite framework. The closest C...O approach is 3.76 Å to an O(3) ion (see Figures 2 and 4). The hydrogen atoms would therefore also be too far from the nearest oxide ions to interact with them, even if the C-H...O angle were linear. Since the energy of the interaction between ethylene and Ag<sup>+</sup> is not considered great enough to cause an appreciable deviation of the hydrogen atoms from the best ethylene plane, C-H...O should be quite bent (see Figure 4) and the hydrogens should be far indeed, more than 3.0 Å, from their nearest oxide neighbors.

The result that ethylene does not displace Ag<sub>6</sub> as a ligand to six Ag<sup>+</sup> ions, and that NH<sub>3</sub> in forming N<sub>3</sub>H<sub>3</sub> and N<sub>3</sub>H<sub>5</sub> does,<sup>4</sup> indicates that the ligand strength of Ag<sub>6</sub> is between those of ethylene and the triazanes with respect to Ag<sup>+</sup>. This conclusion is, of course, strictly valid only for the coordination numbers and geometries involved.

The partial oxidation of ethylene by oxygen to form ethylene oxide is commercially done using silver on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as the catalyst.<sup>27</sup> Proposals for the mechanism of this reaction involve the formation of silver ions. It is likely that Ag<sup>+</sup> ions complexed to zerovalent silver atoms are at the active sites of this catalyst, and that such complexes are particularly oxidizable or reducible for a limited number of electrons, so as to facilitate net reactions showing partial oxidation. Such a partial oxidation reaction, involving ammonia and an unidentified oxidizing agent, has occurred to form the triazanes<sup>4</sup> within a single crystal of zeolite A which contained (Ag<sup>+</sup>)<sub>8</sub>(Ag<sub>6</sub>) complexes.

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**Supplementary Material Available:** Listings of the observed and calculated structure factors (Supplementary Table I) (4 pages). Ordering information is given on any current masthead page.

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# Mercury in Organic Chemistry. 14.<sup>1</sup> A Convenient Regiospecific Synthesis of $\pi$ -Allylpalladium Compounds via Vinylmercurials<sup>2</sup>

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**Abstract:** Vinylmercuric chlorides readily react with palladium chloride, lithium chloride, and alkenes in tetrahydrofuran at 0 °C to give excellent yields of  $\pi$ -allylpalladium compounds. This reaction is especially valuable for the regiospecific synthesis of a wide range of functionally substituted  $\pi$ -allylpalladium compounds. The stereochemistry of these compounds is established by NMR spectral analysis. The mechanism of the reaction presumably involves the addition of a vinylpalladium species to the alkene, followed by a palladium hydride rearrangement to form the  $\pi$ -allylpalladium complex.

$\pi$ -Allylpalladium compounds were first reported in 1957.<sup>6</sup> Since that time a number of procedures have been reported for the synthesis of these compounds.<sup>7-10</sup> At present the most useful general methods of preparing these compounds appear to be the direct allylic hydrogen substitution of alkenes by palladium salts,<sup>11-15</sup> the insertion of palladium(0) reagents into the carbon-halogen bond of allylic halides,<sup>16-19</sup> and the addition of aryl- and certain alkylmercurials to 1,3-dienes.<sup>20</sup> While the first method is certainly one of the most useful approaches to  $\pi$ -allylpalladium compounds because of the ready availability of alkenes, it sometimes suffers due to difficulties in predicting and controlling the regioselectivity of the palladation of unsymmetrical alkenes. Palladium insertion into allylic halides overcomes this disadvantage, but requires as starting materials allylic halides which are generally much more difficult to prepare and handle than alkenes. The palladium-promoted addition of organomercurials to 1,3-dienes also provides a reasonably general route to  $\pi$ -allylpalladium compounds, but is limited to only certain organomercurials and gives low yields. With rapidly increasing interest in the application of  $\pi$ -allylpalladium compounds in organic synthesis,<sup>13-15</sup> new methods of synthesis have become desirable. We wish at this time to report the details of our own novel, regiospecific route to  $\pi$ -allylpalladium compounds via vinyl-

mercurials, which appears to have a number of advantages over previous methods.

## Results and Discussion

**Reaction Conditions.** Our recent work has concentrated on the development of new synthetic organic procedures employing vinylmercurials. These studies have provided new routes to  $\alpha,\beta$ -unsaturated acids,<sup>21</sup> esters,<sup>21</sup> and ketones,<sup>22</sup> as well as butenolides.<sup>23</sup> We have also developed methods for the convenient synthesis of symmetrical<sup>24</sup> and unsymmetrical<sup>25</sup> 1,3-dienes and 1,4-dienes.<sup>26</sup> The latter procedure utilizes the palladium-catalyzed coupling of vinylmercurials and allylic halides (eq 1). This reaction appears to involve the addition of

