

The Crystal Structure of Dehydrated Fully Ag⁺-Exchanged Zeolite A Successively Treated with Ethylene and Bromine Vapor

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The crystal structure of an ethylene sorption complex of dehydrated Ag₁₂-A reacted with bromine vapor has determined by single-crystal X-ray diffraction techniques in the cubic space group of *Pm* $\bar{3}$ *m* at 22(1) °C (*a*=12.180(2) Å). The crystal was prepared by dehydration of Ag₁₂-A at 400 °C and 2×10⁻⁶ Torr for 2 days, followed by exposure to 200 Torr of ethylene gas at 24(1) °C for 1 hr. After the ethylene gas was evacuated for 1 hr, the crystal was exposed to 180 Torr of bromine vapor at 24(1) °C for 1.5 h. The structure was refined to the final error indices, R₁=0.066 and R₂ (weighted)=0.055, using 137 independent reflections for which *I*>3σ(*I*). About 55% of the sodalite unit contain two 6-ring Ag⁺ ions and the remaining 45% contain Ag₆ molecules complexed to 2 Ag⁺ ions at 6-ring sites to give (Ag⁺)₂(Ag₆). Upon sorption of ethylene, 4.75 ethylene molecules were sorbed per unit cell and of these, only 1.25 ethylene molecules were brominated by treatment of dibromine because of the limitation of the available space for the reaction products in the large cavity. In the large cavity, each of 3.5 Ag⁺ ions forms a lateral π complex with an ethylene molecule. About 2.5 8-ring Ag⁺ ions per unit cell interact with 1.25 1,2-dibromoethane and each of ca. 1.25 6-ring Ag⁺ ions also interacts with one of bromine atoms of 1,2-dibromoethane. Each bromine atom approaches a carbon atom with C-Br(1)=2.07(20) Å and C-Br(2)=2.07(10) Å, respectively.

Introduction

The structural informations of various sorbates in the inner surface of the zeolite A have been obtained by the very powerful crystallographic method. The environments of guest molecules such as Cl₂,¹⁻³ Br₂,^{4,5} I₂,^{6,7} C₂H₄,^{8,9} C₂H₆,¹⁰⁻¹³ and CH₃OH¹⁴ have been studied.

In the structure of an ethylene sorption complex of Ag₁₂-A,¹⁰ about 54% of the unit cells have the following arrangement: one 6-ring Ag⁺ ion is in the sodalite unit, and seven others are recessed ca. 1.2 Å into the large cavity where each forms a lateral π complex with an ethylene molecule. These latter Ag⁺ ions are in a near tetrahedral environment, 2.49(1) Å from three framework oxide ions and 2.54(8) Å from each carbon of an ethylene molecule. Two additional Ag⁺ cations are associated with 8-oxygen rings. The remaining 46% contain, in the sodalite unit, the octahedral molecule Ag₆ complexed to six Ag⁺ cations at 6-ring sites to give (Ag⁺)₂(Ag₆).

The crystal structure of a bromine complex of dehydrated fully Ag⁺-exchanged zeolite A has been reported.⁵ In this structure, it was found that approximately 6 bromine molecules were sorbed per unit cell. About 2.4 bromine molecules approach framework oxide ions axially by a charge transfer mechanism. The remaining 3.6 bromine molecules form similar charge transfer complexes with framework oxide ions and each of these molecules interacts weakly with two Ag⁺ ions which it approaches laterally.

This work was initiated to study crystallographically an intrazeolitic reaction among Ag⁺ ions, ethylene, and bromine molecules. It was also hoped to learn the geometry and chemical bonds of the resultant sorption complexes.

Experimental Section

Crystals of zeolite 4A were prepared by Charnell's method.¹⁵

Single crystal about 80 μm on an edge was lodged each in its own fine Pyrex capillary. AgNO₃ (0.05 M) was allowed to flow past the crystal at velocity of approximately 0.5 cm/s for 3 days at 24(1) °C. The clear, colorless, hydrated Ag⁺-exchanged crystal was dehydrated at 400 °C and 2×10⁻⁶ Torr for 2 days. After the dehydrated Ag₁₂-A was cooled to room temperature, the crystal was treated with zeolitically dried ethylene at a pressure of 200 Torr at 24(1) °C for 1 h. After this condition was maintained for 1 h, the ethylene gas was evacuated at 24(1) °C for 1 h. Still under vacuum, the crystal in its capillary with the bromine in a break-off seal tube was removed from the vacuum system by torch. Microscopic examination showed that the crystal became drab green. To prepare the bromine complex, the crystal was treated with zeolitically dried Br₂ vapor at 24(1) °C (180 Torr) for 1.5 h. The crystal in its bromine atmosphere was sealed in its capillary by torch. The crystal became dark black after exposure to bromine vapor.

The cubic space group *Pm* $\bar{3}$ *m* (no systematic absences) was used throughout this work for reasons discussed previously.^{16,17} 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. Molybdenum radiation (*K*_{α1}, λ=0.70930 Å; *K*_{α2}, λ=0.71359 Å) was used for all experiments. The unit cell constants at 22(1) °C, as determined by least-squares refinement of 25 intense reflections of which 19°<2θ<24°, was 12.180(1) Å. Reflections from two intensity-equivalent regions of reciprocal space (*hkl*, 0≤*h*≤*k*≤*l* and *lhk*, 0≤*l*≤*h*≤*k*) were examined using the ω-2θ scan technique. The data were collected using variable scan speeds. Most reflections were observed at slow scan speeds, ranging between 0.136 and 0.323° min⁻¹ in ω. The intensities of three reflections in diverse regions of reciprocal space were recorded every three hours to monitor crystal and X-ray source stability. Only small random fluctuations of these check reflections

Table 1. Positional, Thermal, and Occupancy Parameters of Ag₁₂-A·3.5C₂H₄·1.25C₂H₄Br₂

Atom	Wyc./Pos.	x	y	z	β_{11}^b or B_{110}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy ^d	
											varied	fixed
(Si, Al)	24(k)	0	1827(6)	3666(6)	26(4)	14(4)	18(4)	0	0	20(10)	24.0 ^e	
O(1)	12(h)	0	2060(20)	5000	40(20)	10(20)	40(20)	0	0	0	12.0	
O(2)	12(i)	0	2990(10)	2990(10)	30(20)	-5(9)	-5(9)	0	0	20(30)	12.0	
O(3)	24(m)	1137(9)	1137(9)	3280(10)	70(9)	70(9)	10(10)	70(30)	30(20)	30(20)	24.0	
Ag(1)	8(g)	1370(20)	1370(20)	1370(20)	70(10)	70(10)	70(10)	110(30)	110(30)	110(30)	1.05(6)	1.10
Ag(2)	8(g)	1900(10)	1900(10)	1900(10)	9(8)	9(8)	9(8)	0(20)	0(20)	0(20)	1.02(5)	0.90
Ag(3)	8(g)	2390(4)	2390(4)	2390(4)	51(2)	51(2)	51(2)	45(8)	45(8)	45(8)	4.60(4)	4.75
Ag(4)	6(e)	0	0	1637(7)	40(4)	40(4)	-10(7)	0	0	0	2.50(4)	2.70
Ag(5)	12(i)	0	4280(40)	4280(40)	21(4) ^f						1.17(8)	1.25
Ag(6)	24(h)	0	4140(30)	5000	9(2)						1.16(7)	1.25
C	24(m)	2780(90)	3680(50)	3680(50)	11(5)						8.86(89)	9.50
Br(1)	48(n)	1300(100)	4100(100)	4500(100)	13(6)						1.35(16)	1.25
Br(2)	24(f)	2700(100)	3200(100)	5000	22(6)						1.21(16)	1.25

^aPositional and anisotropic thermal parameters are given $\times 10^4$. Numbers in parentheses are the esd's in the units of the least significant digit given for the corresponding parameter. ^bThe anisotropic temperature factor = $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. ^cIsotropic thermal parameters in units of \AA^2 . ^dOccupancy factors are given as the number of atoms or ions per unit cell. ^eOccupancy for (Si)=12; occupancy for (Al)=12.

were noted during the course of data collection. For each region of reciprocal space, the intensities of all lattice points for $2\theta < 70^\circ$ were recorded. The raw data from each region were corrected for Lorentz and polarization effects including the effect 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 programs, PAINT and WEIGHT.¹⁹ Of the 861 pairs of reflections gathered for the crystal, only the 137 unique reflections for which $I > 3\sigma(I)$ were used in subsequent structure determinations. An absorption correction ($\mu R = ca. 0.40$) was judged to be negligible and was not applied.

Structure Determination

Full-matrix least-squares refinement was initiated with the atomic parameters of the framework atoms [(Si, Al), O(1), O(2) and O(3)] of dehydrated Ag_{5.6}K_{0.4}-A.²⁰ This model converged with an R_1 index, $\sum(|F_o - |F_c||) / \sum F_o$, of 0.49 and a weighted R_2 index, $(\sum w(F_o - |F_c|)^2 / \sum wF_o^2)^{1/2}$, of 0.59.

A difference Fourier function served to reveal the positions of Ag⁺ ions at Ag(3) and Ag(4) (see Table 1). Refinement including these Ag⁺ ions converged to $R_1 = 0.19$ and $R_2 = 0.21$. Successive difference Fourier synthesis revealed the Ag⁺ ion at Ag(2), with peak height 6.5(3) e \AA^{-3} . This model converged at $R_1 = 0.15$ and $R_2 = 0.17$. Successive difference Fourier synthesis revealed three more Ag⁺ positions at Ag(1), Ag(5), and Ag(6). Refinement including these Ag⁺ ions converged to $R_1 = 0.10$ and $R_2 = 0.09$. From a subsequent difference Fourier synthesis, C, Br(1), and Br(2) atoms (see Table 1) were located. The carbon atoms of the ethylene molecules appeared at (0.33, 0.33, 0.33) with a peak height of 1.4(9) e \AA^{-3} . But this position gave a large isotropic thermal parameter 32(5) \AA^2 . Hence a trial refinement with carbon at the 24 fold position (x, z, z) resulted in an opportunity

to select a more satisfactory C-C bond length (1.55(10) \AA) and provided a smaller isotropic thermal parameter 11(5) \AA^2 . This model converged at $R_1 = 0.078$ and $R_2 = 0.069$. Including Br atom at Br(1) in this model lowered the error indices to $R_1 = 0.074$ and $R_2 = 0.064$. Refinement including Br atoms at Br(1) and Br(2) converged to $R_1 = 0.066$ and $R_2 = 0.056$. The occupancy numbers at Br(1) and Br(2) refined to ca. 1.35(16) and 1.21(16) bromine atoms, respectively. These were reset and fixed at 1.25. It is reasonable that these occupancies should be equal because the distance involved indicates that these positions represent the positions of the sorption complex between 1,2-dibromoethane and Ag⁺ ions (see Table 3 and 4). The carbon position of CH₂BrCH₂Br should be different from that of CH₂CH₂ but this could not be resolved crystallographically. The least-squares refinement with the occupancies fixed at the values shown in Table 1 converged to $R_1 = 0.066$ and $R_2 = 0.055$ (the structure was refined to $R_1 = 0.079$ and R_2 (weighted) = 0.056 using 164 independent reflections for which $I > 2\sigma(I)$). The final difference function was featureless.

All crystallographic calculations were done using the MOLEN (a structure determination package programs) supplied by Enraf-Nonius. 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 $\sigma(F)$, its standard deviation. The "goodness-of-fit" are minimized to 3.66, $[\sum w(F_o - |F_c|)^2 / \sum (m - s)]^{1/2}$ where m is the number of observations ($m = 137$ for $I > 3\sigma(I)$ or $m = 164$ for $I > 2\sigma(I)$) and s is the number of variables in least-squares refinement ($s = 51$). Atomic scattering factors for Ag⁺, Ag⁰, C⁰ (valence), Br⁰, O⁻, and (Si, Al)^{1.75+} 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.^{21,22} The final structural parameters and selected interatomic distances and angles are presented in Tables 1 and 2, respectively.

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

(Si, Al)-O(1)	1.65(1)
(Si, Al)-O(2)	1.64(1)
(Si, Al)-O(3)	1.69(1)
Ag(1)-O(3)	2.36(2)
Ag(2)-O(3)	2.14(2)
Ag(3)-O(3)	2.42(1)
Ag(4)-O(3)	2.80(1)
Ag(5)-O(1)	2.84(5)
Ag(5)-O(2)	2.21(4)
Ag(6)-O(1)	2.53(5)
Ag(6)-O(2)	2.82(2)
Ag(2)-Ag(4)	3.28(1)
Ag(4)-Ag(4)	2.82(1)
Ag(3)-C	2.27(5)
C-C	1.55(10)
C-Br(1)	2.07(20)
C-Br(2)	2.07(10)
Ag(3)-Br(2)	3.36(6)
Ag(5)-Br(1)	3.00(10)
Ag(6)-Br(2)	3.50(20)
O(1)-(Si, Al)-O(2)	110.0(8)
O(1)-(Si, Al)-O(3)	111.1(7)
O(2)-(Si, Al)-O(3)	107.0(4)
O(3)-(Si, Al)-O(3)	110.5(6)
(Si, Al)-O(1)-(Si, Al)	160(1)
(Si, Al)-O(2)-(Si, Al)	150.1(7)
(Si, Al)-O(3)-(Si, Al)	137.9(9)
O(3)-Ag(1)-O(3)	102.9(6)
O(3)-Ag(2)-O(3)	119.8(4)
O(3)-Ag(3)-O(3)	99.7(4)
O(3)-Ag(4)-O(3)	59.2(3)
Ag(2)-Ag(4)-Ag(2)	89.5(3)
Ag(3)-C-C	70(3)
C-Ag(3)-C	40(3)
O(3)-Ag(3)-C	105(2)

Discussion

In the ethylene complex of dehydrated $\text{Ag}_{12}\text{-A}$ reacted with bromine vapor, 1.1 Ag^+ ions at Ag(1), 0.9 Ag^+ ion at Ag(2), and 4.75 Ag^+ ions at Ag(3) occupy 6-ring sites on the 3-fold axes of unit cell. Of these ions, 0.9 Ag^+ ion at Ag(2) lies close to its 6-ring plane and 1.1 Ag^+ ions at Ag(1) lie inside of the sodalite cavity, 0.96 Å from (111) plane of O(3)'s. The ions at Ag(3) are recessed *ca.* 1.2 Å into the large cavity. 3.5 Ag^+ ions at Ag(3), each forms a lateral π complex with an ethylene molecule. These Ag^+ ions at Ag(3) are in a near tetrahedral environment, 2.42(1) Å from three framework oxide ions and 2.27(5) Å from each carbon atom of an ethylene molecule. The Ag(3)-C bond length, 2.27(5) Å, indicates that the ethylene is firmly held by the Ag^+ ions at Ag(3). The Ag(3)-O(3) bond is approximately the same length as that (2.49(1) Å) in the structure of an ethylene sorption complex of the dehydrated $\text{Ag}_{12}\text{-A}^{10}$ (see Table 2 and 3). About 1.25 Ag^+ ions on threefold axes get close to bromine atom

Table 3. Deviations of Atoms (Å) from (111) Plane at O(3)^a

O(2)	0.30(1)
Ag(1)	-1.02(1)
Ag(2)	0.10(1)
Ag(3)	1.14(0)
Ag(4)	-2.76(1)
C	3.23(7)
Br(1)	3.05(13)
Br(2)	3.79(14)

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

at Br(2) (Ag(3)-Br(2)=3.36(6) Å). Similar interaction between Ag^+ ions and bromine atoms, 3.36(15) Å to 3.53(5) Å, were also observed in the previous work.⁵

The Ag(4) position is very similar to that of the neutral silver atoms in the structure of dehydrated $\text{Ag}_{12}\text{-A}$.²³ The distance between Ag(4) and its nearest framework oxygens O(3), *ca.* 2.80 Å (see Table 2), is much longer than the sum of the ionic radii, Ag^+ and O^- , $1.26+1.32=2.58$ Å. The distance between Ag(2)-Ag(4), 3.28(1) Å, is too short to be an unmoderated $\text{Ag}^+\text{-Ag}^+$ contact, and too long to be an $\text{Ag}^0\text{-Ag}^0$ bond. Therefore, Ag(2)-Ag(4) distance must be an $\text{Ag}^0\text{-Ag}^+$ coordination contact distance. The silver species at Ag(4) must be reduced silver atoms, Ag^0 .

1.25 Ag^+ ions at Ag(5) and Ag(6) are associated with 8-ring oxygens, respectively. These positions are located in the plane of the 8-rings but not at centers so that favorable approaches to framework oxygens may be made. Ag^+ ions at Ag(5) are 2.84(5) Å and 2.21(4) Å from O(1) oxygens and O(2)'s, respectively. The distances of Ag(6)-O(1) and Ag(6)-O(2) are 2.53(5) Å and 2.82(2) Å, respectively. The 45% of the unit cells in this structure contained Ag_6 in their sodalite units (see Table 4). As the hexasilver molecule changes its coordination number from the eight or six to two, its Ag-Ag bond length (the edge length of the octahedron) decreases from 2.92(2) Å¹⁰ in $(\text{Ag}_6)(\text{Ag}^+)_8$, 2.850(4) Å in $(\text{Ag}_6)(\text{Ag}^+)_6$, and 2.82(1) Å of the present work in $(\text{Ag}_6)(\text{Ag}^+)_2$. This change is consistent with the diminished ability of the two Ag^+ ions to pull up bonding electron density from the hexasilver molecule by coordination. The electron rich Ag_6 molecule can act as a stronger base when it is a ligand to fewer Ag^+ ions. These results agree well with those reported previously.¹⁰ The $\text{Ag}^+\text{-Ag}^0$ interaction, 3.28(1) Å, is somewhat less than the corresponding 3.33(1) Å approach in $(\text{Ag}^+)_6(\text{Ag}_6)^0$ because the more electron rich Ag_6 molecule can be a better base to the two Ag^+ ions to which it is a ligand (see Figure 2).

The remaining 55% of the sodalite units which do not contain Ag_6 molecules hold two Ag^+ ions at Ag(1) (see Table 4). The distance between Ag^+ ions at Ag(1) and framework oxygens O(3) is 2.36(2) Å, a little shorter than the sum of ionic radii of Ag^+ and O^{2-} , 2.58 Å.

Carter *et al.* have studied the sorption of ethylene at room temperature onto a series of ion-exchanged synthetic near-faujasites by infrared spectroscopy and by microcalorimetry.²⁴ They found that ethylene molecules form laterally held π complexes of symmetry C_2 . Of the transition metal ions exa-

Table 4. Inferred Unit Cell Compositions

Composition (%)	Nonframework atoms									Fractional Formula
	6-ring Ag ⁺ ion (sodalite cavity) Ag(1)	6-ring Ag ⁺ ion (sodalite cavity) Ag(2)	6-ring Ag ⁺ ion (large cavity) Ag(3)	Ag ⁺ atom Ag(4)	8-ring Ag ⁺ ion Ag(5)	8-ring Ag ⁺ ions Ag(6)	C	Br(1)	Br(2)	
20	0	2	5	6	1	1	10	1	1	$10Ag^+ \cdot 2H^+ \cdot (Ag^0)_6 \cdot 4C_2H_4 \cdot C_2H_4Br_2 \cdot A^e$
25	0	2	4	6	2	2	8	2	2	$10Ag^+ \cdot 2H^+ \cdot (Ag^0)_6 \cdot 2C_2H_4 \cdot 2C_2H_4Br_2 \cdot A$
55	2	0	5	0	1	1	10	1	1	$9Ag^+ \cdot 3H^+ \cdot 4C_2H_4 \cdot C_2H_4Br_2 \cdot A$
Total occupancy number per unit cell	1.1	0.9	4.75	7	1.25	1.25	9.5	1.25	1.25	

^eA stands for $(Si_{12}Al_{12}O_{46})^{-12}$

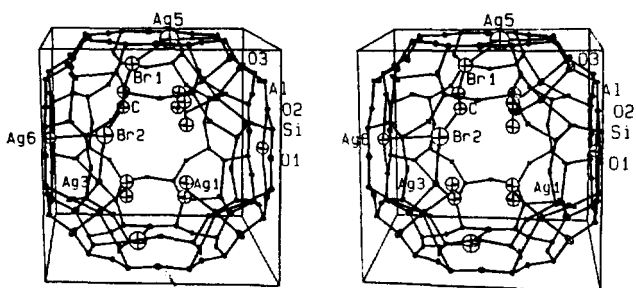


Figure 1. The unit cell of an ethylene sorption complex of dehydrated $Ag_{12}A$ reacted with bromine vapor is shown in stereoview. About 55% of the sodalite units are surrounded by five C_2H_4 complexes. Ellipsoids of 25% probability are used.

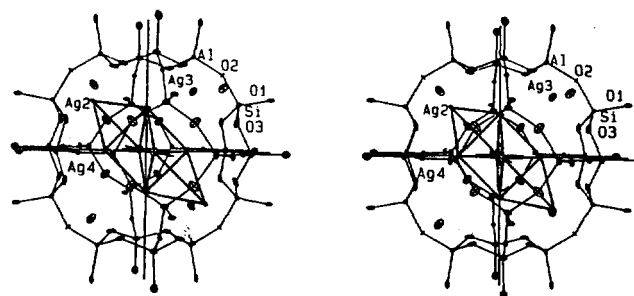


Figure 2. A stereoview of a sodalite unit containing an octahedral Ag_6 molecule complexed to two Ag^+ ions is shown. Ellipsoids of 25% probability are used.

mined, Ag^+ and Cd^{2+} were found to hold ethylene most strongly. Ethylene can readily be removed by evacuation at room temperature, unless the ion involved is Ag^+ or Cd^{2+} . Furthermore, in every complexes except that with Ag^+ , the bound ethylene molecules are found to rotate about the C_2 axis.

The length of $Ag(3)-O(3)$ bonds has increased from 2.25 Å in dehydrated $Ag_{12}A$ to 2.42(1) Å in this structure as the coordination of Ag^+ ion has changed from trigonal to near tetrahedral, an increase of coordination number by one.

The bonding between the Ag^+ ion at $Ag(3)$ and ethylene can be described in terms of the Chatt-Dewar model.²⁵ This bond is formed between the filled π orbital of the ethylene and an empty σ -acceptor orbital of the Ag^+ (5s orbital). Accumulated negative charge on the metal then is "back-donated" by d (or dp hybrid) π orbitals of the metal to a π -acceptor orbital of the alkene, an effect which not only strengthens the preliminary σ bond but synergically reinforces the π bond as well (see Figure 2). 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 carbon positions of CH_2BrCH_2Br can not be equivalent to that of ethylene. Accordingly the carbons position herein reported should be averaged one of those two.

Bromine atoms have been found at two different crystallo-

graphic sites. Bromine atoms at Br(1) and Br(2) can not be an isolated dibromine molecule because the possible bonding distance between Br(1) and Br(2) is either 2.12 Å and 2.57 Å. These distances are either too short or too long for the isolated dibromine considering the bond distance of free dibromine is 2.29 Å. The distances of Br(1)-C and Br(2)-C are 2.07(20) Å and 2.07(10) Å, respectively. Therefore, 1.25 dibromine molecules must be bound to carbon atoms of ethylene. These distances are somewhat longer than the bond distance of Br to C (1.94 Å) in C_2H_5Br .²⁶ Bromine atoms at Br(1) and Br(2) are also bound to Ag^+ ions at $Ag(5)$ and $Ag(6)$. The bond lengths of Br(1)- $Ag(5)$ and Br(2)- $Ag(6)$ are 3.00(10) Å and 3.50(20) Å, respectively. These distances are similar to the sum of the van der Waals radius of Br^0 and the ionic radius of Ag^+ ion, 3.21 Å. Bromine atom at Br(2) was also weakly bound to one Ag^+ ion at $Ag(3)$ (see Figure 3).

In zeolite 4A, the van der Waals diameter of the large cavity is approximately 11.4 Å, and that of the sodalite cavity 6.6 Å.²⁷ The void volumes are ca. 775 and 150 Å³, respectively. The distance between Ag^+ at (0.7610, 0.7610, 0.7610) and Ag^+ at (0.2390, 0.2390, 0.2390) on diagonal line of a large cavity is ca. 11.0 Å which may be considered as a diameter of free space in the large cavity. Therefore, the radius of the remaining sphere excluding Ag^+ ions is 4.24 Å [(11.0 Å - 2 × 1.26 Å (van der Waals radius of Ag^+))/2]. The remaining volume of a large cavity is ca. 319 Å³ ($4/3 \times 3.14 \times 4.24^3$). The shape of ethylene is a cuboid with width 4.24 Å [$2 \times (1.2$

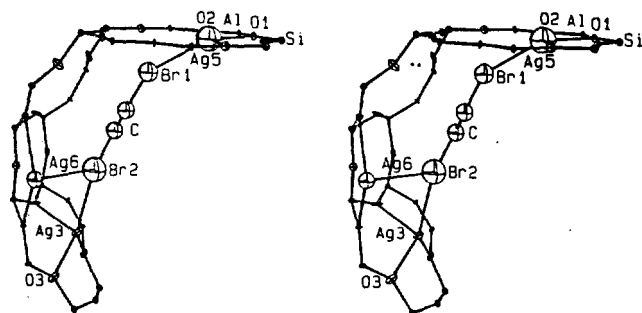


Figure 3. A stereoview of one corner of the large cavity. A $\text{CH}_2\text{Br}-\text{CH}_2\text{Br}$ molecule coordinated to Ag^+ atoms at Ag(3), Ag(5), and Ag(6) is shown. The hydrogen atoms whose positions were not determined, are not shown. Ellipsoids of 25% probability are used.

(van der Waals radius of H) + 1.08 (C-H bond length) \times sin ($117^\circ \times 2$)], length 4.87 \AA [1.34 (C-C bond length) + 2×1.2 (van der Waals radius of H) + $2 \times (1.08$ (C-H bond length) \times sin($121.5^\circ - 90^\circ$))], and breadth 2.4 \AA [2×1.2 (van der Waals radius of H)].²⁸ The volume of one C_2H_4 molecule is therefore ca. 49.6 \AA^3 ($4.24 \times 4.87 \times 2.4$). Consequently, the volume of ethylene molecules is about 236 \AA^3 [$49.6 \text{ \AA}^3 \times 4.75$ (no. of C_2H_4 molecules in the large cavity)]. So, the remaining volume of the large cavity is ca. 83 \AA^3 . In the final result, only 2.5 bromine atoms found in the large cavity. The volume of two bromine atoms is 62 \AA^3 [$2 \times 3/4 \times 3.14 \times 1.95^3$ (van der Waals radius of Br)]. Therefore, the large cavity is effectively filled with ethylene molecules, Ag^+ ions, and 1,2-dibromoethanes (see Figure 3). Because of limitation of the available space occupying the resultant reaction products in large cavity, only 1.25 ethylene molecules were brominated in this structure.

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