

# Crystal Structure of an Ethylene Sorption Complex of Fully Vacuum-Dehydrated Fully Ag<sup>+</sup>-Exchanged Zeolite X (FAU). Silver Atoms Have Reduced Ethylene To Give CH<sub>2</sub><sup>2-</sup> Carbanions at Framework Oxide Vacancies

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The crystal structure of an ethylene sorption complex of fully vacuum-dehydrated fully Ag<sup>+</sup>-exchanged zeolite X (FAU),  $a = 24.865(2)$  Å, has been determined by single-crystal X-ray diffraction techniques in the cubic space group  $Fd\bar{3}$  at 21 °C. It is very different from the ethylene complex of Ag<sub>92</sub>-X that had been dehydrated at 400 °C in flowing oxygen, as were the two dehydrated structures. The crystal was prepared by ion exchange in a flowing stream of aqueous 0.05 M AgNO<sub>3</sub> for 3 days, followed by dehydration at 400 °C and  $2 \times 10^{-6}$  Torr for 2 days, followed by exposure to 300 Torr of zeolitically dry ethylene gas for 2 h at 21 °C. The structure was determined in this atmosphere and was refined using all data to the final error indices (based upon the 534 reflections for which  $F_o > 4\sigma(F_o)$ )  $R_1 = 0.062$  and  $wR_2 = 0.135$ . In this structure, per unit cell, 14 Ag<sup>+</sup> ions were found at the octahedral site I (Ag–O = 2.611(9) Å), and 32 partially reduced Ag<sup>+</sup> ions fill two different site I' positions deep in the sodalite cavities (Ag–O = 2.601(13) and 2.618(12) Å). The sodalite cavities host two different cationic silver clusters. In about 47% of sodalite units, eight silver atoms form interpenetrating tetrahedra, Ag<sub>8</sub><sup>n+</sup> ( $n = 4$  is suggested), with  $T_d$  symmetry. The other 53% of the sodalite units host *cyclo*-Ag<sub>4</sub><sup>m+</sup> ( $m = 2$  is suggested) cations with near  $S_4$  symmetry. These clusters are very similar to those in vacuum-dehydrated Ag<sub>92</sub>-X. Thirty-two Ag<sup>+</sup> ions fill the single 6-rings, 15 at site II' (Ag–O = 2.492(10) Å), and 17 at site II (Ag–O = 2.460(9) Å). The latter 17 lie in supercages where each forms a lateral  $\pi$ -complex with an ethylene molecule. In turn, each C<sub>2</sub>H<sub>4</sub> molecule forms two cis electrostatic hydrogen bonds to framework oxygens. The remaining 14 Ag<sup>+</sup> ions occupy three different II' sites. Vacuum dehydration had caused substantial decomposition: per unit cell, 30 of the 92 Ag<sup>+</sup> ions were reduced and 15 of the 384 framework oxide ions were oxidized to O<sub>2</sub>(g), leaving lattice vacancies. The sorption of C<sub>2</sub>H<sub>4</sub> at 21 °C reoxidized about 7 of the 30 Ag<sup>0</sup> atoms to Ag<sup>+</sup> and reduced 1.75 ethylene molecules to give CH<sub>2</sub><sup>2-</sup> groups which refilled 3.5 of these 15 lattice vacancies. The remaining vacancies may have been filled with H<sub>2</sub>C=C<sup>2-</sup> ions. The unit cell formula, which originally contained 384 oxygen atoms, may be [Ag<sub>92</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>17</sub>][Si<sub>100</sub>Al<sub>92</sub>O<sub>369</sub>-(CH<sub>2</sub>)<sub>3.5</sub>] or [Ag<sub>92</sub>H<sub>23</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>17</sub>][Si<sub>100</sub>Al<sub>92</sub>O<sub>369</sub>(CH<sub>2</sub>)<sub>3.5</sub>(C<sub>2</sub>H<sub>2</sub>)<sub>11.5</sub>].

## Introduction

Zeolites are high-capacity sorbents and effective catalysts. Because of their uniform channel systems, they are highly selective for both functions. A knowledge of the molecule–zeolite and molecule–molecule interactions within the zeolite is crucial to understanding the mechanisms involved. In addition to its framework structure, the nature of the zeolite depends on the exchangeable cations that are generally present, their chemical nature, their distribution over the available sites, and the interactions that these cations can have with sorbed (guest) molecules.<sup>1</sup> Variations in the chemical composition of the zeolite framework, including defects in its structure, are also often important.

Dispersions of silver ions and atoms are effective as catalysts. For example, catalysts containing both Ag<sup>0</sup> and Ag<sup>+</sup> are important in partial oxidation processes such as the formation of ethylene oxide from ethylene and oxygen.<sup>1</sup> As another

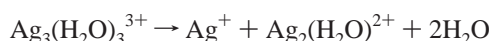
example, Ag<sup>+</sup>-exchanged zeolite Y (FAU) has been reported to be capable of cleaving water into hydrogen and oxygen<sup>2</sup> by a photochemically induced reduction of Ag<sup>+</sup>, followed by the oxidative thermal desorption of hydrogen.

Exchangeable transition-metal ions in evacuated zeolites are generally coordinatively unsaturated. Accordingly, they complex readily with a variety of guest molecules. Their complexes with CO,<sup>3</sup> CS<sub>2</sub>,<sup>4</sup> C<sub>2</sub>H<sub>2</sub>,<sup>5–7</sup> C<sub>2</sub>H<sub>4</sub>,<sup>8–14</sup> C<sub>3</sub>H<sub>6</sub>,<sup>15–17</sup> CH<sub>3</sub>NH<sub>2</sub>,<sup>18,19</sup> C<sub>6</sub>H<sub>6</sub>,<sup>20,21</sup> C<sub>9</sub>H<sub>12</sub>,<sup>22</sup> NO,<sup>23,24</sup> NO<sub>2</sub>,<sup>23</sup> N<sub>2</sub>O<sub>4</sub>,<sup>24</sup> sulfur (disproportionated),<sup>25</sup> and iodine (disproportionated)<sup>26</sup> have been observed crystallographically.

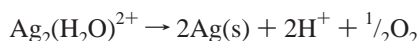
By infrared spectroscopy and microcalorimetry, Carter et al. studied the sorption of ethylene at room temperature onto a series of transition metal ion-exchanged synthetic near-faujasites.<sup>27</sup> They reported that C<sub>2</sub>H<sub>4</sub> molecules form laterally held complexes of symmetry C<sub>2</sub>. Of the transition metal ions examined, Ag<sup>+</sup> and Cd<sup>2+</sup> were found to hold C<sub>2</sub>H<sub>4</sub> most strongly; furthermore, except in their complexes with Ag<sup>+</sup> and Cd<sup>2+</sup>, the sorbed ethylene molecules were reported to be rotating freely.

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Kim and Seff found  $(\text{Ag}^+)_8(\text{Ag}_6)$  clusters, octahedral hexa-silver molecules each coordinated to eight silver ions, in the sodalite units of vacuum-dehydrated fully  $\text{Ag}^+$ -exchanged zeolite A (LTA).<sup>28</sup> In this structure,  $\text{Ag}^+$  ions were found to be reduced by the following reactions that occurred within the sodalite units.<sup>28</sup> The penultimate step of the dehydration process,



is followed by



The resulting silver atoms then aggregated, and the hydrogen ions, with oxide ions abstracted from the zeolite framework to leave lattice vacancies, left the structure as  $\text{H}_2\text{O}(\text{g})$ , together with the  $\text{O}_2(\text{g})$ .

In the structure of  $\text{Ag}_{4.6}\text{Na}_{7.4}\text{-A}$ , which had been vacuum dehydrated and treated with  $\text{H}_2$  at 350 °C,  $(\text{Ag}_6)^{3+}$  clusters of low symmetry were found in the large cavities.<sup>29</sup>

$(\text{Ag}^+)_6(\text{Ag}_6)$  clusters were found in the sodalite cavities of an ethylene sorption complex<sup>9</sup> of partially decomposed fully  $\text{Ag}^+$ -exchanged zeolite A.<sup>28</sup> In addition, per unit cell, 3.6  $\text{Ag}^+$  ions were recessed approximately 1.1 Å into large cavity where each formed a lateral  $\pi$ -complex with an ethylene molecule. These  $\text{Ag}^+$  ions have a nearly tetrahedral environment, considering  $\text{C}_2\text{H}_4$  to be monodentate, 2.49(1) Å from three framework oxygens and 2.54(8) Å from each carbon atom of an ethylene molecule ( $\text{C}-\text{C} = 1.19(12)$  Å).

In the structures of  $\text{M}_{46}\text{-X}\cdot n\text{C}_2\text{H}_4$  ( $n \approx 30$ ;  $\text{M} = \text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Mn}^{2+}$ ),<sup>12–14</sup> each  $\text{M}^{2+}$  ion at site II has moved 0.11–0.50 Å further into the supercage from the plane of the three oxygens to which it is bound, as compared to empty  $\text{M}_{46}\text{-X}$ , to coordinate laterally to an ethylene molecule in the supercage.

A review of silver chemistry and structure in zeolites is available.<sup>30</sup>

More recently, the crystal structure of  $\text{Ag}_{86}\text{Si}_{100}\text{Al}_{92}\text{O}_{369}$  (FAU),  $\text{Ag}_{86}\text{-X}$ , with distorted cubic  $\text{Ag}_8^{n+}$  and *cyclo*- $\text{Ag}_4^{m+}$  clusters ( $n = 4$  and  $m = 2$  were proposed) filling its sodalite cavities, and with 15 lattice-oxygen vacancies per unit cell (assuming these  $n$  and  $m$  values), was reported.<sup>31</sup> The formula of the zeolite phase is given; the six silver atoms per unit cell that left the zeolite phase to deposit on the crystal surface are excluded from this formula. To give this complex result,  $\text{Ag}_{92}\text{-Si}_{100}\text{Al}_{92}\text{O}_{384}$  (FAU),  $\text{Ag}_{92}\text{-X}$ , had simply been vacuum-dehydrated at 400 °C.

In an attempt to prevent the intrazeolitic reduction of  $\text{Ag}^+$ , to give a far simpler material for further sorption experiments,  $\text{Ag}_{92}\text{-X}$  was dehydrated in flowing oxygen at 400 °C, highly oxidizing conditions, followed by cooling in the same flowing oxygen. This procedure successfully produced fully dehydrated  $\text{Ag}_{92}\text{Si}_{100}\text{Al}_{92}\text{O}_{384}$ ,  $(\text{Ag}^+)_{92}\text{-X}$ . Thereafter its ethylene sorption complex,  $(\text{Ag}^+)_{92}\text{-X}\cdot 27\text{C}_2\text{H}_4$ , was prepared and its structure determined.<sup>32</sup> In this complex, 12  $\text{Ag}^+$  ions per unit cell were found at the octahedral site I and 16  $\text{Ag}^+$  ions occupy the nearby site-I' positions; weak  $\text{Ag}^+\cdots\text{Ag}^+$  bonding was seen. Thirty-two  $\text{Ag}^+$  ions fill the single 6-rings, 27 at site II and 5 at site II', and the remaining 32  $\text{Ag}^+$  ions occupy four different III' sites. Each of the 27 site-II  $\text{Ag}^+$  ions extends 1.08 Å into the supercage to form a strong lateral  $\pi$ -complex with an ethylene molecule.

This work was done to study the effect of  $\text{C}_2\text{H}_4$  sorption on the  $\text{Ag}_8^{n+}$  and *cyclo*- $\text{Ag}_4^{m+}$  clusters that were present in the sodalite cavities of  $\text{Ag}_{86}\text{-X}$ .<sup>31</sup> Such sorption had previously resulted in the conversion of  $(\text{Ag}^+)_8(\text{Ag}_6)^{28}$  to  $(\text{Ag}^+)_6(\text{Ag}_6)^9$  with

TABLE 1: Summary of Crystallographic Data

crystal color	dark yellow
data collection $T$ (°C)	21
scan technique	$\theta$ -2 $\theta$
radiation (Mo K $\alpha$ ) $\lambda_1/\lambda_2$ (Å)	0.70930/0.71359
unit cell constant, $a$ (Å)	24.865(2)
unit cell constant $T$ (°C)	21
2 $\theta$ range for $a$ (deg)	14–22
no. of reflections for $a$	25
2 $\theta$ range in data collection (deg)	3 < 2 $\theta$ < 50
no. of unique reflections ( $m$ )	1104
no. of reflections with $F_o > 4\sigma(F_o)$	534
no. of parameters ( $s$ )	92
data/parameter ratio ( $m/s$ )	12.2
weighting parameters: $a/b$	0.098/433.4
$R_1^a/wR_2^b$ ( $F_o > 4\sigma(F_o)$ )	0.062/0.135
$R_1^a/wR_2^b$ (all data)	0.214/0.173
goodness of fit <sup>c</sup>	1.035

<sup>a</sup>  $R_1 = \sum |F_o| - |F_c| / \sum F_o$ . <sup>b</sup>  $wR_2 = [\sum (F_o^2 - F_c^2)^2 / \sum (F_o^2)^2]^{1/2}$ .  
<sup>c</sup> Goodness-of-fit =  $[\sum (F_o^2 - F_c^2)^2 / (m - s)]^{1/2}$ . All data were used.

shortened  $\text{Ag}-\text{Ag}$  bonds in zeolite A. It was also done to locate the sorbed  $\text{C}_2\text{H}_4$  molecules, and to determine the shifts of the  $\text{Ag}^+$  ions upon sorption, including their possible redistribution among sites. The oxidation of surface silver atoms by ethylene to give  $\text{CH}_2^{2-}$  groups which would occupy oxide vacancies in the zeolite lattice was unanticipated.

## Experimental Section

**Crystal Preparation.** Large single crystals of zeolite Na-X (FAU), stoichiometry  $\text{Na}_{92}\text{Si}_{100}\text{Al}_{92}\text{O}_{384}$  per unit cell, were prepared in Leningrad, now St. Petersburg, Russia.<sup>33</sup> One of these, a colorless octahedron about 0.2 mm in cross-section, was lodged in a fine Pyrex capillary. An aqueous 0.05 M solution of  $\text{AgNO}_3$  (Aldrich, 99.9999%) was allowed to flow past the crystal at a velocity of 1.0 cm/s for 3 days. The capillary containing the crystal was attached to a vacuum system, and the crystal was cautiously dehydrated by gradually increasing its temperature (ca. 25 °C/h) to 400 °C at a constant pressure of  $2 \times 10^{-6}$  Torr. Finally, the system was maintained at this state for 2 days. A crystal, so prepared, had been observed to be dark gray.<sup>31</sup> The crystal was then treated with 300 Torr of ethylene gas (Aldrich, 99.5%) for 2 h at 21 °C. This gas had been zeolitically dried and purified in situ by an in-series 16-cm tube of zeolite 5A beads that had themselves been fully dehydrated in situ and chilled for a few minutes in a Dewar flask of liquid nitrogen. The resulting dark yellow crystal, still in its ethylene atmosphere, was sealed in its capillary by torch.

**X-ray Data Collection.** The cubic space group  $Fd\bar{3}$  was used. This choice is suggested by the low Si/Al ratio which requires, at least in the short range, alternation of Si and Al. It is supported by the inequality seen between the  $hkl$  and  $khl$  reflection intensities and the observation, in the final structure, that the Si-O bond lengths are all less than those of Al-O. 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. The unit cell constant, determined by a least-squares refinement of 25 intense reflections, is  $a = 24.865(2)$  Å. All unique reflections in the positive octant of an  $F$ -centered unit cell for which  $2\theta < 50^\circ$ ,  $l \geq h$ , and  $l \geq k$  were recorded. Calculations were performed with XCAD4 (LP corrections)<sup>34</sup> and with the structure determination program package, SHELX97.<sup>35</sup> Absorption corrections, which had little effect on the final  $R$  indices, were made empirically using a  $\psi$  scan.<sup>36</sup> Other details are the same as those previously reported.<sup>31,32</sup> Table 1 provides a summary of the experimental and crystallographic data.

TABLE 2: Positional, Thermal, and Occupancy Parameters<sup>a</sup>

atom	Wyc.		x	y	z	<sup>b</sup> $U_{11}$ or <sup>c</sup> $U_{iso}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$	<sup>d</sup> occupancy	
	pos	site										varied	fixed
Si	96(g)		−509(1)	1247(2)	363(1)	154(18)	157(17)	145(17)	−34(17)	3(15)	18(19)		96
Al	96(g)		−517(1)	375(1)	1236(2)	142(19)	143(19)	140(18)	−6(16)	−5(18)	−37(19)		96
O(1)	96(g)		−1036(4)	2(4)	996(4)	294(54)	349(60)	315(57)	−106(51)	−80(45)	−197(53)		96
O(2)	96(g)		2(4)	−18(4)	1482(4)	380(58)	330(54)	215(46)	170(50)	−45(49)	−118(49)		96
O(3)	96(g)		−242(4)	745(4)	700(4)	273(54)	253(54)	268(56)	64(46)	87(44)	44(44)		96
O(4)	96(g)		−737(3)	797(4)	1735(4)	153(49)	212(51)	261(54)	13(43)	72(43)	−122(41)		96
Ag(1)	16(c)	I	0	0	0	309(9)	309(9)	309(9)	−3(9)	−3(9)	−3(9)	13.6(2)	14
Ag(2a)	32(e)	I'	804(9)	804(9)	804(9)	427(63)	427(63)	427(63)	35(66)	35(66)	35(66)	14.6(2)	15
Ag(2b)	32(e)	I'	773(16)	764(16)	986(9)	264(117)	279(103)	390(109)	−81(62)	−187(112)	−79(108)	15.5(4)	17
Ag(3)	32(e)	II'	1848(1)	1848(1)	1848(1)	411(13)	411(13)	411(13)	103(14)	103(14)	103(14)	14.8(2)	15
Ag(4)	32(e)	II	2469(1)	2469(1)	2469(1)	304(10)	304(10)	304(10)	17(11)	17(11)	17(11)	17.2(2)	17
Ag(5)	96(g)	III'	4036(18)	1057(18)	1427(18)	854(134)						4.7(3)	4
Ag(6)	96(g)	III'	4172(14)	645(14)	911(15)	741(94)						5.9(3)	5
Ag(7)	96(g)	III'	4187(15)	1596(15)	1941(15)	773(96)						5.3(3)	5
C	96(g)		2820(56)	2931(67)	3254(43)	2449(739)						34.5(3)	34
H(1) <sup>e</sup>	96(g)		2511	2695	3230								34
H(2) <sup>e</sup>	96(g)		2890	3075	3610								34

<sup>a</sup> The space group is  $Fd\bar{3}$  with origin chosen at the center of symmetry. Positional and anisotropic thermal parameters are given  $\times 10^4$ . Numbers in parentheses are the esds in the units of the least significant digit given for the corresponding parameter. <sup>b</sup> The anisotropic temperature factor =  $\exp[-2\pi^2(a^2 U_{11}h^2 + U_{22}k^2 + U_{33}l^2 + U_{12}hk + U_{13}hl + U_{23}kl)]$ . <sup>c</sup>  $B_{iso} = 8\pi^2 U_{iso}$ . <sup>d</sup> Occupancy factors are given as the number of atoms or ions per unit cell. Four or more (4 + x) Si atoms<sup>55</sup> are present at the Al position per unit cell; x Al atoms may therefore be at the Si position; x may be zero. <sup>e</sup> Hydrogen atom positions were calculated<sup>35</sup> with a C–H distance of 0.97 Å.

## Structure Determination

Full-matrix least-squares refinement<sup>35</sup> was done on  $F^2$  using all reflections. It was initiated with the atomic parameters of the framework atoms [Si, Al, O(1), O(2), O(3), and O(4)] in  $\text{Ag}_{86}\text{--X}$ .<sup>31</sup> These positions when refined isotropically yielded  $R_1 = 0.48$  and  $wR_2 = 0.80$ . For the definitions of  $R_1$  and  $wR_2$ , see the footnotes to Table 1.

A Fourier difference electron-density function yielded two strong peaks at (0.0, 0.0, 0.0) and (0.249, 0.249, 0.249) with heights of 21 and 13  $\text{e} \text{ \AA}^{-3}$ , respectively. Isotropic refinement including them as Ag(1) and Ag(4), respectively, converged to  $R_1 = 0.39$  and  $wR_2 = 0.73$  with occupancies of 13.8(11) and 16.6(14).

A difference Fourier function based on the above model revealed two peaks at (0.083, 0.083, 0.083) and (0.186, 0.186, 0.186) with heights of 16 and 11  $\text{e} \text{ \AA}^{-3}$ , respectively. Inclusion of these peaks as ions at Ag(2a) and Ag(3) lowered the error indices to  $R_1 = 0.11$  and  $wR_2 = 0.23$ . The occupancy numbers at Ag(2a) and Ag(3) had refined to 27.6(5) and 13.8(13), respectively.

One peak with height 2.5  $\text{e} \text{ \AA}^{-3}$  appeared at (0.078, 0.077, 0.103) on the next difference Fourier function. Including it as Ag(2b) and allowing it to refine isotropically led to convergence with  $R_1 = 0.087$  and  $wR_2 = 0.202$  with an occupancy of 15.5(4).

A subsequent difference Fourier function revealed three additional peaks at (0.416, 0.071, 0.160), (0.418, 0.040, 0.087), and (0.419, 0.163, 0.188) with heights of 2.4, 1.2, and 1.1  $\text{e} \text{ \AA}^{-3}$ . Allowing them to refine isotropically as ions at Ag(5), Ag(6), and Ag(7), respectively, lowered the error indices to  $R_1 = 0.070$  and  $wR_2 = 0.150$ . The occupancies refined to 4.7(3) at Ag(5), 5.9(3) at Ag(6), and 5.3(3) at Ag(7).

Anisotropic refinements of the framework and Ag positions, except Ag(5), Ag(6), Ag(7) which were refined isotropically, converged with  $R_1 = 0.062$  and  $wR_2 = 0.136$ .

The carbon position (0.284, 0.293, 0.327) with a peak height of 1.2  $\text{e} \text{ \AA}^{-3}$  was seen on the next difference Fourier function. It was stable when refined isotropically, and the error indices decreased to  $R_1 = 0.061$  and  $wR_2 = 0.133$ .

The occupancy numbers at the Ag positions and C were fixed as shown in Table 1 by the assumption of stoichiometry, the

requirement of neutrality, and the observation that the occupancies at Ag(4) and C were refining in the ratio of 1:2. The final error indices converged to  $R_1 = 0.062$  and  $wR_2 = 0.135$ .

Fixed weights were used initially; the final weights were assigned using the formula  $w = q/[\sigma^2(F_o^2) + (aP)^2 + bp + d + e\sin(\theta)]$ , where  $p = fF_o^2 + (1 - f)F_c^2$ , to give  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bp]$ , where  $p = (F_o^2 + 2F_c^2)/3$ ; the  $a$  and  $b$  parameters were refined in least squares (see Table 1). The final difference function was featureless; in particular, no electron density was seen near the  $\text{Ag}^+$  ions at the III' sites. Atomic scattering factors<sup>37</sup> for Si, Al, O,  $\text{Ag}^+$ , and C were used. All scattering factors were modified to account for anomalous dispersion.<sup>38,39</sup> The final structural parameters, and selected interatomic distances and angles, are presented in Tables 2 and 3, respectively.

## Discussion

Zeolite X is a synthetic Al-rich analogue of the naturally occurring mineral faujasite (FAU). Its structure, including the sites that cations usually occupy, is shown in Figure 1. Further description is available.<sup>14,17,18,40</sup>

In this structure, the Ag atoms and ions are found at eight crystallographic sites (a large number): I, two different I', II, II', and three different III' sites (see Table 2). In contrast, Ag atoms and ions occupied fewer sites (five: I, I', II, II', and III') in  $\text{Ag}_{86}\text{--X}$ .<sup>31</sup>

The 14  $\text{Ag}^+$  ions at Ag(1) are each coordinated octahedrally by six O(3) oxygen atoms at site I, at the centers of the D6Rs (see Figure 2). The  $\text{Ag}^+\text{--O}$  distances are all 2.611(9) Å, approximately equal to the sum of the conventional ionic radii of  $\text{Ag}^+$  and  $\text{O}^{2-}$ ,  $1.26 + 1.32 = 2.58 \text{ \AA}$ ,<sup>41</sup> indicative of a reasonably good fit.

Fifteen Ag atoms or ions at Ag(2a) and another seventeen at Ag(2b) fill the 32-fold site I', in the sodalite cavities opposite the D6Rs (see Figures 2 and 3). Each atom or ion at Ag(2a) and Ag(2b) is recessed 1.74 and 1.87 Å, respectively, into the sodalite cavity from its 6-ring plane (Table 4). The distances between Ag(2a) and its three nearest framework oxygens at O(3) are 2.618(12) Å; for Ag(2b) the shortest distance is 2.601(13) Å. These distances are less than the  $\text{Ag}^0$  atom to framework oxygen distance, 2.78 Å, in previous studies,<sup>28,42</sup> yet (perhaps)

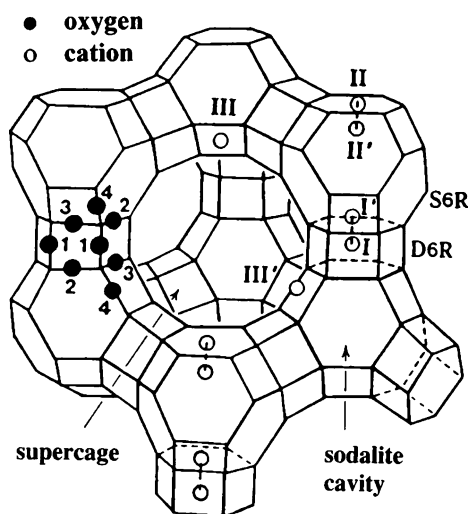


**TABLE 3: Selected Interatomic Distances (Å) and Angles (deg)<sup>a</sup>**

distance		angle	
Si—O(1)	1.602(9)	O(1)—Si—O(2)	111.9(6)
Si—O(2)	1.624(9)	O(1)—Si—O(3)	110.1(5)
Si—O(3)	1.643(10)	O(1)—Si—O(4)	108.3(5)
Si—O(4)	1.614(9)	O(2)—Si—O(3)	104.6(5)
mean	1.621	O(2)—Si—O(4)	110.8(5)
Al—O(1)	1.699(9)	O(3)—Si—O(4)	111.1(5)
Al—O(2)	1.728(10)	O(1)—Al—O(2)	112.6(5)
Al—O(3)	1.759(10)	O(1)—Al—O(3)	108.3(5)
Al—O(4)	1.715(9)	O(1)—Al—O(4)	110.2(5)
mean	1.725	O(2)—Al—O(3)	105.9(5)
		O(2)—Al—O(4)	109.2(5)
		O(3)—Al—O(4)	110.6(5)
Ag(1)—O(3)	2.611(9)		
Ag(2a)—O(3)	2.618(12)		
Ag(2b)—O(3)	2.601(13)	Si—O(1)—Al	145.5(7)
Ag(3)—O(2)	2.492(10)	Si—O(2)—Al	135.2(6)
Ag(4)—O(2)	2.460(9)	Si—O(3)—Al	128.9(5)
Ag(5)—O(4)	2.66(8)	Si—O(4)—Al	139.9(5)
Ag(6)—O(1)	2.69(8)		
Ag(6)—O(4)	2.38(4)	O(3)—Ag(1)—O(3)	98.9(5)
Ag(7)—O(1)	2.62(5)	O(3)—Ag(2a)—O(3)	80.8(4)
Ag(7)—O(4)	2.43(4)	O(3)—Ag(2b)—O(3)	81.4(4)
Ag(2a)—Ag(2a)	3.14(3)	O(2)—Ag(3)—O(2)	92.8(3)
Ag(2a)—Ag(3)	2.650(9)	O(2)—Ag(4)—O(2)	94.4(3)
Ag(2b)—Ag(2b)	2.71(7)/2.75(7)	O(1)—Ag(7)—O(4)	62.1(9)
Ag(2a)—Ag(1)	3.462(6)		
Ag(2b)—Ag(1)	3.615(5)	Ag(2a)—Ag(3)—Ag(2a)	72.7(7)
Ag(3)—Ag(4), v <sup>c</sup>	2.674(6)	Ag(3)—Ag(2a)—Ag(3)	104.9(5)
Ag(4)—C	2.43(8)	Ag(2b)—Ag(2b)—Ag(2b)	76.6(7)
C—C	1.37(11)		
C—H(1)	0.97 <sup>b</sup>		
C—H(2)	0.97 <sup>b</sup>		
H(1)···O(4)	3.12 <sup>b</sup>		

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

<sup>b</sup> Hydrogen positions were calculated.<sup>35</sup> <sup>c</sup> v = virtual.



**Figure 1.** Stylized drawing of the framework structure of zeolite X. Near the center of each line segment is an oxygen atom. The nonequivalent oxygen atoms are indicated by the numbers 1 to 4 representing O(1) to O(4). Silicon and aluminum atoms alternate at the tetrahedral intersections in the short range, except that Si must substitute for at least 4% of the Al atoms. Extra framework cation positions are labeled with Roman numerals.

more than the sum of the ionic radii of  $\text{Ag}^+$  and  $\text{O}^{2-}$ , 2.58 Å ( $\text{Ag}^+$  to  $\text{O}^{2-}$  distances in zeolites are often far shorter than this sum; see for example  $\text{Ag(3)—O(2)}$  and  $\text{Ag(4)—O(2)}$  in this work (see Table 3)).<sup>43</sup> Accordingly, the Ag species at  $\text{Ag(2a)}$  and  $\text{Ag(2b)}$  are not easily identified as  $\text{Ag}^0$  or  $\text{Ag}^+$ .

Typical Ag—O distances between 3-fold-axis  $\text{Ag}^+$  ions and three framework oxygens in zeolite A are 2.25(2) Å;<sup>44</sup> similar

**TABLE 4: Deviations (Å) of Atoms from Six-Ring Planes**

	$\text{Ag}_{86}\text{—X}$		cation site	this work	
	position	displacement		position	displacement
at O(2) <sup>a,b</sup>	Ag(3)	−1.28	II'	Ag(3)	−1.37
	Ag(4)	0.76	II	Ag(4)	1.31
				C	3.60
at O(3) <sup>b,c</sup>	Ag(1)	−1.65	I	Ag(1)	−1.73
	Ag(2a)	1.76	I'	Ag(2a)	1.74
	Ag(2b)	2.00	I'	Ag(2b)	1.87

<sup>a</sup> A positive displacement indicates that the atom or ion lies in the supercage. <sup>b</sup> Sites I' and II' are in the sodalite units. <sup>c</sup> The negative displacement indicates that the ion lies within a double six-ring.

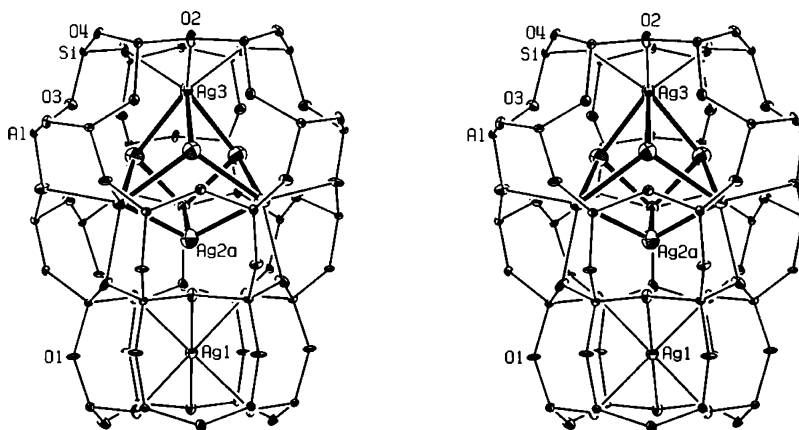
Ag—O distances, 2.231(11) Å, are seen between site-II  $\text{Ag}^+$  ions and three framework oxygens in vacuum-dehydrated  $\text{Ag}_{86}\text{—X}$ .<sup>31</sup> On the other hand, typical  $\text{Ag}^0$  to three framework oxygen distances in zeolite A are 2.78 Å.<sup>28,42</sup> The present 3-fold-axis Ag—O distances, 2.618(12), 2.601(13), and 2.492(10) Å, are intermediate, indicating that the Ag species at  $\text{Ag(2a)}$ ,  $\text{Ag(2b)}$ , and  $\text{Ag(3)}$  are partially reduced.

The distance between  $\text{Ag(2a)}$  and  $\text{Ag(3)}$ , 2.650(9) Å, is too short to be a nonbonded intercationic distance. It is close to the sum of the ionic radius of  $\text{Ag}^+$  and the atomic radius of Ag metal, 2.705 Å.<sup>30</sup> The  $\text{Ag(2a)—O(3)}$  distance, 2.618(12) Å, is longer than  $\text{Ag(3)—O(2)}$ , 2.492(10) Å, suggesting that  $\text{Ag(2a)}$  is more reduced than  $\text{Ag(3)}$ . Four  $\text{Ag(2a)}$  and four  $\text{Ag(3)}$  atoms form a tetrahedrally distorted cube (two interpenetrating tetrahedra) as shown in Figure 2. These  $\text{Ag}_8^{n+}$  clusters ( $n < 8$ ) occupy 47% of the sodalite cavities and are stabilized by charge delocalization from Ag atoms to  $\text{Ag}^+$  ions ( $\text{Ag(2a)}$  to  $\text{Ag(3)}$ ). The interaction between framework oxygens and Ag species, predominantly between O(2) and  $\text{Ag(3)}$ , must also contribute to the stabilization of these clusters.

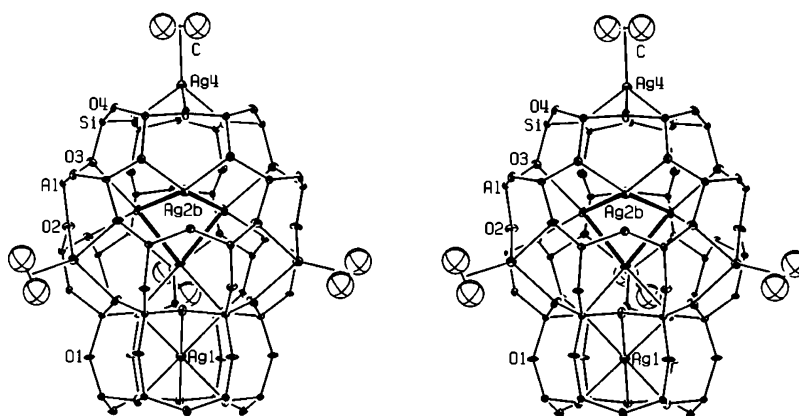
In the other 53% of the sodalite cavities, four  $\text{Ag(2b)}$  atoms or ions form bent *cyclo*- $\text{Ag}_4$  clusters (see Figures 3 and 4). The  $\text{Ag(2b)—Ag(2b)}$  distances are 2.71(7) and 2.75(7) Å. The mean of these two distances, 2.73 Å, is again almost the same as the sum of the  $\text{Ag}^+$  and  $\text{Ag}^0$  radii, 2.705 Å.<sup>30</sup> This *cyclo*- $\text{Ag}_4^{m+}$  ( $m < 4$ ) cluster nearly has  $S_4$  symmetry. All angles are 76.6(7)°.

In the present structure, the distances  $\text{Ag(2a)—O(3)}$  (2.618(12) Å),  $\text{Ag(2b)—O(3)}$  (2.601(13) Å), and  $\text{Ag(3)—O(2)}$  (2.492(10) Å) are very similar to the corresponding bond distances in vacuum-dehydrated  $\text{Ag}_{86}\text{—X}$ <sup>31</sup> (2.642(10), 2.628(14), and 2.461(11) Å, respectively). This indicates that the present Ag species were reduced to the same degree, at least approximately, as in vacuum-dehydrated  $\text{Ag}_{86}\text{—X}$ . Other Ag to Ag distances are also very similar in the two structures, respectively:  $\text{Ag(2a)—Ag(2a)} = 3.14(3)$  vs  $3.22(3)$  Å;  $\text{Ag(2a)—Ag(3)} = 2.650(9)$  vs  $2.705(6)$  Å; and  $\text{Ag(2b)—Ag(2b)} = 2.71(7)/2.75(7)$  vs  $2.622(14)/2.749(13)$  Å (see Table 3). For these reasons, and because odd electron clusters are uncommon in chemistry, the present clusters may be  $\text{Ag}_4^{2+}$  and  $\text{Ag}_8^{4+}$  as suggested for  $\text{Ag}_{86}\text{—X}$ .<sup>31</sup> Each sodalite cavity in this structure hosts either a  $\text{Ag}_4^{n+}$  or a  $\text{Ag}_8^{m+}$  cluster.

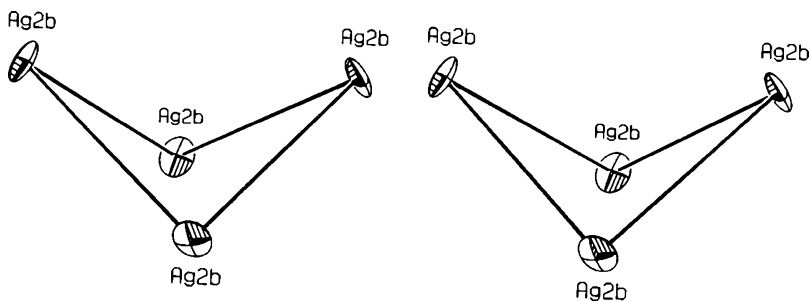
The 32  $\text{Ag}^+$  ions at site II in vacuum-dehydrated  $\text{Ag}_{86}\text{—X}$  redistributed to two different 3-fold-axis  $\text{Ag}^+$  positions upon the sorption of ethylene: 17  $\text{Ag}^+$  ions at site II coordinate to ethylene molecules and 15  $\text{Ag}^+$  ions at site II' do not. The latter (at  $\text{Ag(3)}$ ) each coordinate at 2.497(11) to three O(2) framework oxygens, and are recessed 1.37 Å into the sodalite cavity from their three-O(2) planes (see Figure 2 and Table 4). The 17  $\text{Ag}^+$  ions at  $\text{Ag(4)}$  lie at site II; each of these coordinates to three framework oxygens at 2.460(9) Å and extends 1.31 Å into the supercage where it forms a lateral  $\pi$ -complex with an ethylene molecule. To coordinate to ethylene, each of the 17 site-II  $\text{Ag}^+$



**Figure 2.** Stereoview of a sodalite cavity with one double six-ring attached. One  $\text{Ag}^+$  ion is shown at Ag(1) (site I). Four Ag atoms at Ag(2a) (site I') and four Ag atoms at Ag(3) (site II') form a  $T_d$  (distorted cubic  $\text{Ag}_8^{n+}$  cluster;  $n = 4$  is proposed. About 47% of sodalite units have this arrangement. Ellipsoids of 20% probability are used.



**Figure 3.** Stereoview of a sodalite cavity with one double six-ring attached. One  $\text{Ag}^+$  ion at Ag(1) and four Ag atoms at Ag(2b) are shown. The four at Ag(2b) form *cyclo*- $\text{Ag}_4^{m+}$  clusters;  $m = 2$  is proposed. About 53% of sodalite units have this arrangement. Four  $\text{Ag}^+$  ions at Ag(4) (site II) are shown. Each  $\text{Ag}^+$  ion at Ag(4) coordinates to an ethylene molecule. Ellipsoids of 20% probability are used.



**Figure 4.** Stereoview of *cyclo*- $\text{Ag}_4^{m+}$ ;  $m = 2$  seems most likely. The bond distances are 2.71(7) and 2.75(7) Å. All angles are 76.6(7)°. Ellipsoids of 20% probability are used.

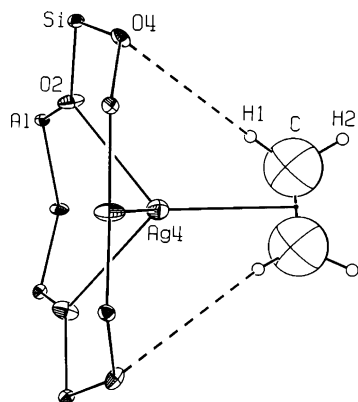
ions has moved  $1.31 - 0.76^{31} = 0.55$  Å along their 3-fold axes more deeply into the supercage from its three-O(2) plane (see Figures 5 and 6 and Table 4). In this way, each of  $\text{Ag}^+$  ions is able to coordinate more tetrahedrally to an ethylene molecule (considering ethylene to be monodentate).

The 34 carbon atoms in this structure (17 molecules of  $\text{C}_2\text{H}_4$ ) are equivalent at Wyckoff position 96(g). The two carbon atoms of each ethylene molecule are equidistant from Ag(4). The center of the C=C bond does not lie on a 3-fold axis of the crystal structure. The Ag(4)–C bond length, 2.43(8) Å, indicates that the ethylene molecule is relatively firmly held by the  $\text{Ag}^+$  ion at Ag(4). Metal cation to ethylene carbon distances in zeolites range from 2.42(10) Å in  $\text{Ag}_{92}$ –X dehydrated in flowing oxygen to 2.98(4) Å (see Table 5).

The bonding between the silver ion at Ag(4) and ethylene can be described in terms of two components according to the

Chatt-Dewar model.<sup>45</sup> A  $\sigma$  component arises from the overlap of a filled ethylene  $\pi$  orbital and a vacant  $\text{Ag}^+$  5s orbital, and a  $\pi$  component occurs by the overlap of the filled 4d orbitals of  $\text{Ag}^+$  with the vacant antibonding  $\pi^*$  orbital of ethylene. By the latter interaction, the C=C bond order may be diminished by back-donation.

Ag(4) is the only Ag position within coordinating distance of  $\text{C}_2\text{H}_4$ .  $\text{Ag}^+$  can coordinate more strongly to  $\text{C}_2\text{H}_4$  than a partially reduced Ag cation can, so the 17 Ag(4) ions that coordinate to  $\text{C}_2\text{H}_4$  should be fully oxidized  $\text{Ag}^+$  cations and not members of reduced clusters. This is further supported by their equal (17) occupancies and the close approach of Ag(4) to framework oxygens (see Table 3). The Ag(4)– $\text{C}_2\text{H}_4$  complexes must share sodalite cavities with the  $\text{Ag}_4^{m+}$  clusters as shown in Figure 3. This is because only four 6-rings are occupied by the atoms of  $\text{Ag}_4^{m+}$  in its sodalite cavity, so the



**Figure 5.**  $\text{Ag}(\text{C}_2\text{H}_4)^+$  complex on the inner surface of a supercage. Seventeen  $\text{Ag}^+$  ions at Ag(4) coordinate to ethylene molecules as shown. Two hydrogen atoms of each ethylene molecule are calculated by SHELX97<sup>35</sup> to interact weakly with O(4) oxygens. Ellipsoids of 20% probability are used.

**TABLE 5: Comparison of Ethylene–Cation Approach Distances in Zeolites A and X**

structure	M–C (Å)	cation radius (Å)	effective ethylene radius (Å)	C=C (Å) <sup>a</sup>	ref
$(\text{Ag}^+)_{92}-\text{X}\cdot 27\text{C}_2\text{H}_4^b$	2.42(10)	1.26	1.16	1.24(15)	32
$\text{Ag}_{92}-\text{X}\cdot n\text{C}_2\text{H}_4^c$	2.43(8)	1.26	1.17	1.37(11)	d
$\text{Ag}_{12}-\text{A}\cdot 3.6\text{C}_2\text{H}_4$	2.54(8)	1.26	1.28	1.19(12)	9
$\text{Cd}_6-\text{A}\cdot 4\text{C}_2\text{H}_4$	2.67(6)	0.97	1.70	1.27(8)	10
$\text{Cd}_{46}-\text{X}\cdot 29.5\text{C}_2\text{H}_4$	2.70(4)	0.97	1.73	1.26(5)	14
$\text{Mn}_{46}-\text{X}\cdot 30\text{C}_2\text{H}_4$	2.76(6)	0.80	1.96	1.10(8)	13
$\text{Ca}_6-\text{A}\cdot 4\text{C}_2\text{H}_4$	2.87(5)	0.99	1.88	1.48(7)	11
$\text{Ca}_{46}-\text{X}\cdot 30\text{C}_2\text{H}_4$	2.98(4)	0.99	1.99	1.39(6)	12

<sup>a</sup> For comparison, the C=C double bond length in  $\text{C}_2\text{H}_4(\text{g})$  is 1.344 Å (ref 46). <sup>b</sup> Dehydrated in flowing oxygen at 400 °C before sorption of  $\text{C}_2\text{H}_4$ . <sup>c</sup> Dehydrated under vacuum at 400 °C before sorption of  $\text{C}_2\text{H}_4$ . <sup>d</sup> This work.

remaining four are available. In contrast, the  $\text{Ag}_{88}^{n+}$  atoms occupy all eight 6-rings in their sodalite cavities.

The imprecisely determined C=C distance, 1.37(11) Å, differs insignificantly from the C=C bond length in ethylene gas, 1.344 Å.<sup>46</sup> In nonzeolitic transition-metal complexes, a broad range of C=C distances (from 1.354(15) to 1.46(2) Å) can be observed.<sup>47</sup>

The positions of the four hydrogen atoms of each ethylene molecule (see Table 2) were calculated with a C–H bond length of 0.97 Å using the software system SHELX97.<sup>35</sup> In each molecule, two cis hydrogen atoms can each be about 3.12 Å from an O(4) framework oxygen (see Figure 5). Thus, each ethylene molecule can form two weak (electrostatic) hydrogen bonds with the anionic zeolite framework; for comparison, the

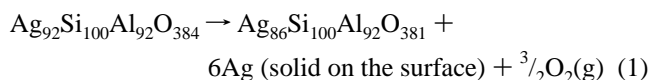
sum of the van der Waals radii of oxygen and hydrogen is 1.4 + 1.2 = 2.6 Å.<sup>48</sup>

The remaining 14  $\text{Ag}^+$  ions (at Ag(5), Ag(6), and Ag(7)) occupy three different III' sites in the supercage with occupancies of 4, 5, and 5, respectively (see Figure 6). Each of these  $\text{Ag}^+$  ions coordinates to only two framework oxygens. Some or all of these may coordinate to additional ethylene molecules which could not be found in this work; this may also be true for  $(\text{Ag}^+)_{92}-\text{X}\cdot 27\text{C}_2\text{H}_4$ .<sup>32</sup>

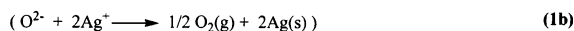
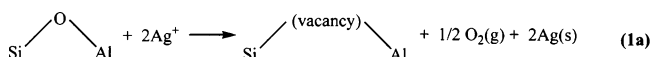
The site occupancies in vacuum-dehydrated  $\text{Ag}_{86}-\text{X}^{31}$  are compared to those in this structure, its ethylene complex, in Table 6. The differences are small except at the III' sites; the additional ca. 7  $\text{Ag}^+$  ions per unit cell have gone there. Unlike vacuum-dehydrated  $\text{Ag}_{86}-\text{X}$ ,<sup>31</sup> in which six silver ions are missing per unit cell and appear to have been reduced and to have migrated to the zeolite surface, all 92 silver atoms or ions are present in this structure.

$(\text{Ag}^+)_{92}-\text{X}\cdot 27\text{C}_2\text{H}_4^{32}$  and the present  $\text{C}_2\text{H}_4$  complex of  $\text{Ag}_{92}-\text{X}$  are both dark yellow. However,  $\text{Ag}_{86}-\text{X}^{31}$  was dark gray. This supports the proposition that Ag atoms left the crystal upon vacuum dehydration to deposit on its surface, and that they left the surface (reentered the crystal as  $\text{Ag}^+$ ) after exposure to  $\text{C}_2\text{H}_4$ .

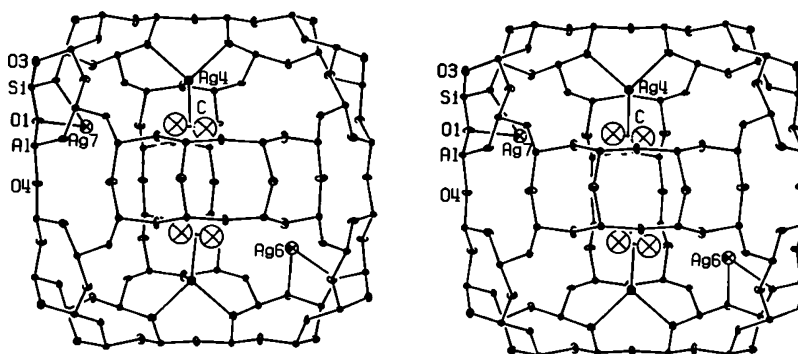
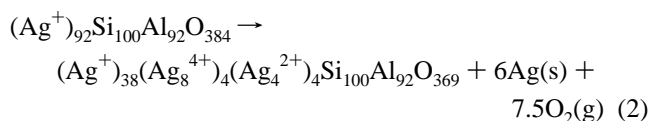
During the vacuum dehydration of hydrated  $\text{Ag}^+$ -exchanged zeolite X,  $(\text{Ag}^+)_{92}-\text{X}$  exclusive of water molecules, the following reaction, much like that which occurred during the vacuum dehydration of  $\text{Ag}^+$ -exchanged zeolite A (LTA),<sup>28</sup> may have occurred:



Locally, the reaction would have been



Many more lattice vacancies were generated as additional silver atoms formed by the same reaction; these did not migrate to the surface, however, but remained within the zeolite structure as members of reduced silver clusters. The complete net reaction upon the vacuum-dehydration of hydrated  $\text{Ag}_{92}-\text{X}$ , assuming that the intrazeolitic reduced clusters are  $\text{Ag}_8^{4+}$  and  $\text{Ag}_4^{2+}$ , would be



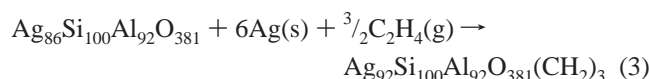
**Figure 6.** Stereoview of a supercage. Two  $\text{Ag}^+$  ions at Ag(4) (site II) are shown. Each  $\text{Ag}^+$  ion at Ag(4) coordinates to an ethylene molecule. One  $\text{Ag}^+$  ion at Ag(6) (site III') and one  $\text{Ag}^+$  ion at Ag(7) (site III') are shown. Ellipsoids of 20% probability are used.

**TABLE 6: Distribution of Ag<sup>+</sup> and Partially Reduced Ag<sup>+</sup> Cations among Sites**

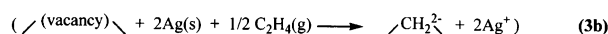
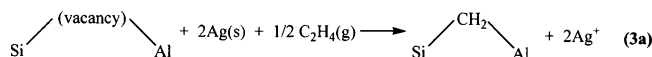
sites	crystal	
	Ag <sub>86</sub> -X <sup>a</sup>	this work
I	16	14
I'	16, 16 <sup>b</sup>	15, 17 <sup>b</sup>
II	16	17
II'	16	15
III'	2, 4 <sup>c</sup>	4, 5, 5 <sup>d</sup>

<sup>a</sup> Reference 31. <sup>b</sup> There are two different I' sites in this structure.<sup>c</sup> There are two different III' sites in this structure. <sup>d</sup> There are three different III' sites in this structure.

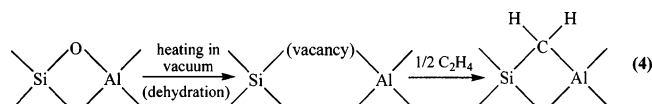
Unlike Ag<sub>86</sub>-X, the present crystal structure has 92 Ag species per unit cell and the number of observed reflections for which  $F_o > 4\sigma(F_o)$  is 532. For comparison, only 320 reflections were observed for Ag<sub>86</sub>-X. A similar loss of crystal data (quality) was seen upon vacuum dehydration in the Ag-A (LTA) system.<sup>28</sup> This indicates that at least some of the lattice vacancies were filled upon exposure to ethylene gas and suggests that the crystal was partially rehabilitated as follows:



Locally, the reaction would be

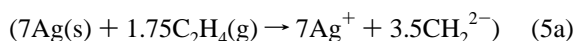
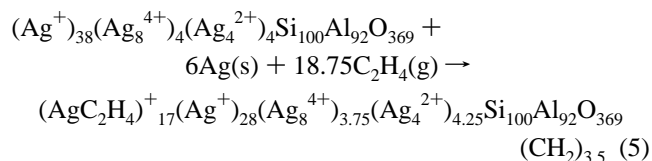


Note that CH<sub>2</sub><sup>2-</sup> is isoelectronic with O<sup>2-</sup>. Altogether, the zeolite framework may lose oxygen atoms during vacuum dehydration and then reconstruct itself with ethylene as follows:

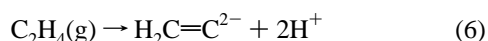


Also, to a small degree at 21 °C, silver atoms from the Ag<sub>8</sub><sup>n+</sup> clusters were oxidized leaving somewhat fewer Ag<sub>8</sub><sup>n+</sup> clusters (47%, down from 50% in Ag<sub>86</sub>-X<sup>31</sup>), somewhat more Ag<sub>4</sub><sup>m+</sup> clusters (53%, up from 50% in Ag<sub>86</sub>-X<sup>31</sup>), and about one more Ag<sup>+</sup> ion per unit cell.

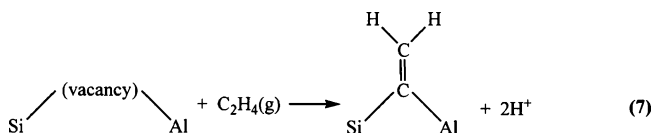
If ethylene reacted with the above zeolite only to coordinate to Ag<sup>+</sup> ions and to oxidize about seven Ag<sup>0</sup> to seven Ag<sup>+</sup> (six Ag<sup>0</sup> from the zeolite surface and the seventh from the reduction of about 3% of the Ag<sub>8</sub><sup>4+</sup> clusters to Ag<sub>4</sub><sup>2+</sup>), only a fraction (3.5/15) of the lattice vacancies would be occupied by CH<sub>2</sub><sup>2-</sup> groups. The following net reaction would have occurred upon exposure of the resulting zeolite to ethylene gas at 21 °C



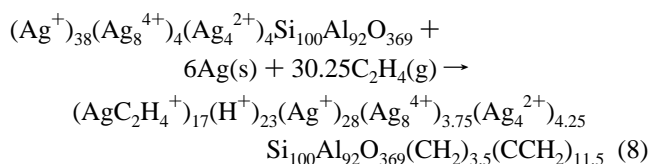
At this point, another reaction may have proceeded to generate carbanions to fill the remaining lattice vacancies:



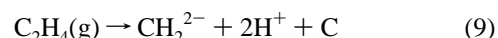
Locally H<sub>2</sub>C=C<sup>2-</sup> groups would add to the zeolite framework as follows:



In addition to the 17 C<sub>2</sub>H<sub>4</sub> molecules that coordinate to site-II Ag<sup>+</sup> ions, 13.25 C<sub>2</sub>H<sub>4</sub> molecules (1.75 as CH<sub>2</sub><sup>2-</sup> (reaction 5a) + 11.5 as C<sub>2</sub>H<sub>2</sub><sup>2-</sup> (reaction 6)) would have added to the zeolite framework per unit cell to fill lattice vacancies. The net reaction per unit cell would then be



Reaction 6 is consistent with the nonblack (dark yellow) color of the crystal. In contrast, the reaction



may be dismissed because the carbon produced would have blackened the crystal.

These results are not entirely novel. Organosilicate chemistry is well established<sup>49</sup> and zeolitic<sup>50,51</sup> and mesoporous materials<sup>52,53</sup> have been reported which contain both oxide and methylene groups<sup>50–52</sup> and methylene groups only.<sup>53</sup> Organic–inorganic hybrid zeolites have been synthesized by partially substituting lattice oxygen atoms with methylene groups.<sup>50</sup> Through various characterization methods such as MAS NMR, the presence of methylene bridges (Si–CH<sub>2</sub>–Si) that replace siloxane bridges (Si–O–Si) has been verified; some of the Si–C bonds were cleaved to give terminal methyl groups. A new class of cage-like oligomers were also found to form by hydrolysis and polycondensation of a methylene-bridged bis-trialkoxysilane precursor in the presence of tetramethylammonium hydroxide, which led to the creation of novel silica-based hybrid materials.<sup>51</sup>

Ethylene may be adding to the zeolite X framework just as O<sub>2</sub>(g) had added to a previous zeolite framework to fill lattice vacancies. Ag–A (LTA) was exposed to H<sub>2</sub>(g) at 330 °C, and water was lost to leave framework vacancies.<sup>30,54</sup> In that case, a larger fraction (6/48 per unit cell = 0.125) of the framework oxygens were lost as compared to the fraction lost in this work (15/384 = 0.039). In that work, the single-crystal diffraction pattern was not simply diminished, but extinguished; the crystal became lustrous black in color, a more extreme color change than we had observed upon vacuum-dehydration of hydrated (Ag<sup>+</sup>)<sub>92</sub>-X, indicating a greater loss of silver, and therefore a greater production of framework vacancies. Upon treatment with O<sub>2</sub>(g) at 330 °C (This elevated temperature may not have been necessary.), the diffraction pattern of that single crystal of zeolite A was fully restored,<sup>54</sup> presumably because the lattice vacancies were largely or fully refilled.

Lattice vacancies were also introduced during attempted dehydrations of Ag–A. This led to the formation of neutral octahedral hexasilver clusters in the sodalite cavities.<sup>28</sup> An inverse relationship was seen between the number of Ag<sup>+</sup> ions reduced and the size of the diffraction data set. The larger the number of Ag<sup>+</sup> ions reduced (the larger the number of lattice vacancies produced, the larger the number of hexasilver clusters



produced), the weaker the single-crystal diffraction pattern. Ultimately, the single-crystal diffraction pattern was lost, as was seen with zeolite A upon treatment with H<sub>2</sub>(g) (see previous paragraph). The full occupancy of the sodalite cavities by hexasilver clusters could not be observed crystallographically because the single-crystal diffraction pattern was lost before this concentration of hexasilver was reached.

In the crystal structure of the ethylene sorption complex of fully dehydrated, fully oxidized, fully Ag<sup>+</sup>-exchanged zeolite X,<sup>32</sup> (Ag<sup>+</sup>)<sub>92</sub>-X, 27 ethylene molecules were sorbed, each coordinating to a Ag<sup>+</sup> ion at site II. No lattice vacancies had been generated and no redox reactions took place. In the present crystal, two kinds of cationic silver clusters, Ag<sub>8</sub><sup>n+</sup> and Ag<sub>4</sub><sup>m+</sup>, fill the sodalite cavities, so there are fewer Ag<sup>+</sup> ions available for complexation. Therefore, only 17 C<sub>2</sub>H<sub>4</sub> molecules were sorbed per unit cell, still at site II. However, the Ag<sup>+</sup> to C<sub>2</sub>H<sub>4</sub> carbon distances are the same: 2.43(8) and 2.42(10) Å, respectively. (The C=C distances (imprecisely determined) are also the same: 1.37(11) and 1.24(15) Å, respectively.) In both of these structures, each ethylene molecule makes two cis electrostatic hydrogen bonds to framework oxygen atoms.

The number of lattice vacancies filled by CH<sub>2</sub><sup>2-</sup> groups (3.5) is approximately equal to the number of excess Si atoms (4) per unit cell. Because of the long-range Si/Al order that this crystal has, this suggests that CH<sub>2</sub><sup>2-</sup> groups only occupy lattice vacancies between two silicon atoms. This assumes that lattice vacancies are generally or never adjacent. Reaction 4 should then contain only Si atoms.

## Summary

Ag<sup>+</sup> ions occupy eight crystallographic sites: I, two I', II', II, and three III' sites. Some sodalite cavities host Ag<sub>8</sub><sup>n+</sup> and the remainder contain Ag<sub>4</sub><sup>m+</sup>; *n* = 4 and *m* = 2 are suggested. The Ag–Ag distances in these clusters, 2.650(9) Å and 2.71(7)/2.75(7) Å, are close to the sum of the ionic radius of Ag<sup>+</sup> (1.26 Å) and the atomic radius of Ag metal (1.445 Å), 2.705 Å.<sup>30</sup> The 17 site-II Ag<sup>+</sup> ions have moved 0.55 Å along their 3-fold axes more deeply into the supercage each to coordinate strongly (laterally) to an ethylene molecule. Each ethylene molecule makes two electrostatic hydrogen bonds to framework oxygen atoms. Ethylene has also oxidized surface silver atoms to give the carbanions CH<sub>2</sub><sup>2-</sup> which occupy some of the lattice vacancies originally occupied by oxide ions. H<sub>2</sub>C=C<sup>2-</sup> carbanions may occupy the remaining lattice vacancies.

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**Supporting Information Available:** Table of calculated and observed structure factors squared with esds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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