

은 이온과 아연 이온으로 치환한 제올라이트 A ($\text{Ag}_{2.8}\text{Zn}_{4.6}\text{-A}$)의 탈수한 결정구조와 이것에 에틸렌을 흡착시킨 결정구조

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Crystal Structures of Dehydrated Ag^+ and Zn^{2+} Exchanged Zeolite A, $\text{Ag}_{2.8}\text{Zn}_{4.6}\text{-A}$ and of Its Ethylene Sorption Complex

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요 약. 탈수한 $\text{Ag}_{2.8}\text{Zn}_{4.6}\text{-A}$ 의 구조와 이 결정에 에틸렌 기체가 흡착된 구조를 X-선 단결정 회절법으로 입방공간군인 $Pm3m$ 을 사용하여 구조를 해석하고 정밀화시켰다. Ag^+ 이온 및 Zn^{2+} 이온으로 이온교환시킨 두 개의 결정을 400°C , 2×10^{-6} Torr의 진공하에서 2일간 탈수시킨 후, 그 중 하나의 결정에는 $25(1)^\circ\text{C}$ 에서 250 Torr의 에틸렌 기체를 1시간 동안 처리하였다. 탈수한 $\text{Ag}_{2.8}\text{Zn}_{4.6}\text{-A}$ ($a = 12.137(2)\text{\AA}$)의 결정구조는 $I > 3\sigma(I)$ 인 237개의 회절점을 사용하여 R_w 값이 0.044까지 정밀화시켰고, 에틸렌을 흡착시킨 $\text{Ag}_{2.8}\text{Zn}_{4.6}\text{-A} \cdot 5.6\text{C}_2\text{H}_4$ ($a = 12.106(2)\text{\AA}$)의 결정구조에서는 301개의 회절점을 사용하여 R_w 값이 0.050까지 정밀화시켰다. 2.8개의 Ag^+ 이온은 에틸렌 분자와 π 착물을 형성하며, 6-링 평면에서 큰 동공쪽으로 $0.922(2)\text{\AA}$ 이동한 위치에 골조의 산소와 $2.240(5)\text{\AA}$ 에서 결합하고 있었고, 에틸렌 분자의 탄소원자와 $2.290(5)\text{\AA}$ 에서 결합하고 있었다. Zn^{2+} 이온은 단위세포당 두 개의 서로 다른 3회 회전축상에 위치하고 있으며, 이 중 2.8개의 Zn^{2+} 이온은 에틸렌 분자와 π 착물을 형성하며, (111) 평면에서 큰 동공쪽으로 $0.408(2)\text{\AA}$ 이동한 위치에 골조의 산소와 결합하고 있었다. Zn^{2+} 이온과 에틸렌 분자의 탄소원자간 결합거리는 $2.78(4)\text{\AA}$ 이며, 이는 비교적 약한 결합임을 나타낸다.

ABSTRACT. Two crystal structures of dehydrated $\text{Ag}_{2.8}\text{Zn}_{4.6}\text{-A}$ and of its ethylene sorption complex have been determined by single-crystal X-ray diffraction techniques. The structures were solved and refined in the cubic space group $Pm3m$ at $23(1)^\circ\text{C}$. Dehydration of two crystals studied were achieved at 400°C and 2×10^{-6} Torr for 2 days and one crystal was treated with 250 Torr of ethylene at $25(1)^\circ\text{C}$. The structures of dehydrated $\text{Ag}_{2.8}\text{Zn}_{4.6}\text{-A}$ ($a = 12.137(2)\text{\AA}$) and of its ethylene sorption complex ($a = 12.106(2)\text{\AA}$) were refined to final error indices, $R(\text{weighted}) = 0.044$ with 237 reflections and $R(\text{weighted}) = 0.050$ with 301 reflections, respectively, for which $I > 3\sigma(I)$. 2.8 Ag^+ ions are recessed $0.922(2)\text{\AA}$ from (111) plane of three 6-ring oxygens into the large cavity where each forms a lateral π complex with an ethylene molecule. These Ag^+ ions are in $2.240(5)\text{\AA}$ from three framework oxide ions and $2.290(5)\text{\AA}$ from each carbon atom of an ethylene molecule. The Zn^{2+} ions occupy two different threefold axis positions of the unit cell. 2.8 Zn^{2+} ions are recessed $0.408(2)\text{\AA}$ from (111) plane of the 6-ring oxygens and each Zn^{2+} ion forms a π complex with an C_2H_4 molecule. The distances between Zn^{2+} ions and carbon atom of ethylene molecule, $\text{Zn}(2) - \text{C} = 2.78(4)\text{\AA}$ are long. This indicates that this bond is relatively weak.

INTRODUCTION

Selective catalysis of a wide variety of organic reactions by zeolites, containing transition metal ions is well established^{1,2}. It has been possible to determine the geometry and symmetry of the weak complexes which form when small molecules (for example, C₂H₄, CO, H₂O)^{3,4} are physically sorbed onto the inner surfaces of the zeolite. As a part of these studies, Carter *et al.*⁵ 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 ethylene molecules form laterally held π complexes of symmetry C₂. Of the transition metal ions examined, Ag⁺ and Cd²⁺ were found to hold ethylene most strongly. Furthermore, in every complexes except that with Ag⁺, the bound ethylene molecules are found to rotate about the C₂ axis.

In the crystal structure of an ethylene sorption complex⁶ of partially decomposed fully Ag⁺-exchanged zeolite A, *ca.* 3.6 Ag⁺ ions per unit cell are recessed approximately 1.1 Å into the large zeolite cavity where each forms a lateral π complex with an ethylene molecule. These 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 atom of an ethylene molecule (which is here counted as a monodentate ligand).

This study was done to learn the selective positions of Ag⁺ and Zn²⁺ ions within zeolite A and to investigate the geometry of the sorbed ethylene molecules which may form a lateral π complex with Ag⁺ ions and/or Zn²⁺ ions.

EXPERIMENTAL SECTION

Crystal of zeolite 4A were prepared by Char-nell's method⁷. Each of two single crystals 0.08 mm on an edge was selected and lodged in a fine glass capillary. To prepare exchanged crystals of composition Ag_{2.8}Zn_{4.6}-A and Ag_{2.8}Zn_{4.6}-A·5.6C₂H₄, an exchange solution of AgNO₃ and Zn(NO₃)₂ in the mole ratio of 1 to 300, with a total concentra-

tion of 0.05 M, was used.

Ion exchange was accomplished by allowing the solution, to flow past each crystal at a velocity of approximately 1.0 cm/sec for 3 days. Then each crystal was dehydrated at 400°C and 2 × 10⁻⁶ Torr for 2 days. After each crystal returned to ambient temperature (*ca.* 24°C), one crystal was sealed in its capillary by a torch. The crystal became brown during the dehydration treatment.

The second crystal was treated with 250 Torr of zeolitically dried ethylene for 1 hr at 25(1)°C. Under these conditions, the crystal in its capillary was removed from the vacuum system by torch.

Microscopic examination indicated that the crystal had become dark brick-red color.

The space group *Pm3m* (no systematic absences) was used throughout this work for reasons discussed previously⁸⁻¹⁰. 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, using Mo K α radiation (K α_1 , λ = 0.70930 Å; K α_2 , λ = 0.71359 Å). The unit cell constant, as determined by a least-squares refinement of 25 intense reflections for which 18° < 2 θ < 25° is 12.137(2) Å for Ag_{2.8}Zn_{4.6}-A and 12.106(2) Å for Ag_{2.8}Zn_{4.6}-A·5.6C₂H₄, respectively.

Reflections from the two intensity equivalent regions of reciprocal space (*hkl*, $h \leq k \leq l$ and *lhk*, $l \leq h \leq k$) were examined. The intensities were measured using ω -2 θ scan technique over a scan width of (0.80 + 0.344 tan θ)° in ω . The data were collected using the variable scan speeds. Most reflections were observed at slow scan speeds, from 0.137° to 0.342° in ω min⁻¹. The intensities of three reflections in diverse regions of reciprocal space were recorded after every 3 hrs to monitor crystal and X-ray source stability. Only small, random fluctuations of these check reflections were noted during the course of data collections. For each region of reciprocal space, the intensities of all lattice points for which 2 θ < 70° were recorded.

The raw data from each region were corrected for Lorentz and polarization effects including that due to incident beam monochromatization; the re-

duced intensities were merged and the resultant estimated standard deviations were assigned to each average reflection by the computer programs, PAINT and WEIGHT¹¹. An absorption correction (μR ca. 0.109, $\rho_{cal}=1.89$ g/cm³ and $F(000)=856$ for $Ag_{2.8}Zn_{4.6}A$, and μR ca. 0.110, $\rho_{cal}=2.05$ g/cm³ and $F(000)=945$ for $Ag_{2.8}Zn_{4.6}A \cdot 5.6C_2H_4$) was judged to be negligible and was not applied^{12,13}. Of the 894 pairs of reflections for $Ag_{2.8}Zn_{4.6}A$ and 892 for $Ag_{2.8}Zn_{4.6}A \cdot 5.6C_2H_4$, only the 237 and 301 pairs, respectively, for which $I > 3\sigma(I)$ were used in subsequent structures determination.

STRUCTURE DETERMINATION

All structure calculations were done using the Structure Determination Package (SDP)¹¹ programs supplied by Enraf-Nonius.

Dehydrated $Ag_{2.8}Zn_{4.6}A$. Least-squares refinement began using the framework atomic coordinates (Si, Al), O(1), O(2), and O(3)) and three 6-ring Ag^+ ions at (0.190, 0.190, 0.190) of dehydrated $Ag_{7.6}Na_{4.4}A^{14}$. The occupancy of Ag^+ ions at Ag(1) refined 2.71(2) (see Table 1). Refinement with isotropic thermal parameters converged to an unweighted R_1 index, $(\sum |F_o - |F_c|| / \sum F_o)$ of 0.196 and a weighted R_2 index, $(\sum w(F_o - |F_c|)^2 / \sum wF_o^2)^{1/2}$ of 0.229.

Since ionic radii of Zn^{2+} and Ag^+ ions are different, $Zn^{2+}=0.74$ Å vs $Ag^+=1.26$ Å, and their atomic scattering factors are also quite different, 28 e^- for Zn^{2+} vs 46 e^- for Ag^+ , it is easy to distinguish Ag^+ from Zn^{2+} ions. Also, the approach distances between those ions and zeolite oxide ions in partially decomposed $Ag_{12}A^6$ and dehydrated $Zn_5K_2A^{15}$ and $Ag_{12-2x}Zn_xA$ ($x=1.46$ and 4.6)¹⁶ have been determined. Besides, the requirement that 12 monovalent cations (or 6 divalent cations) per unit cell be found does not allow the major positions to refine to acceptable occupancies with the alternative assignment of ionic identities¹⁰.

A difference Fourier synthesis revealed two large threefold axis peaks at (0.166, 0.166, 0.166) and (0.210, 0.210, 0.210) with heights of 4.9(2) $e\text{Å}^{-3}$, and 5.9(2) $e\text{Å}^{-3}$ respectively. Two peaks were sta-

ble in least-squares refinement. The first peak was refined to 2.0 Zn^{2+} ions, and the second was to 2.6 Zn^{2+} ions. This model lowered the error indices to $R_1=0.047$ and $R_2=0.046$ (see Table 1). Anisotropic refinement of all atoms converged to $R_1=0.043$ and $R_2=0.044$. The occupancies of Ag(1), Zn(1), and Zn(2) were fixed at the values shown in Table 1. All other parameters were varied except the thermal parameter of Zn(2). Final difference Fourier function was featureless. All shift/error in the final cycle of the least square were less than 0.3% of the their corresponding esd's.

$Ag_{2.8}Zn_{4.6}A \cdot 5.6C_2H_4$. Full-matrix least-squares refinement of the structure was initiated using framework atoms and Ag^+ ions and Zn^{2+} ions, which determined from the previous crystal of $Ag_{2.8}Zn_{4.6}A$. Full anisotropic refinement of this model converged with $R_1=0.068$ and $R_2=0.077$.

From a subsequent difference Fourier map, the carbon atoms of the ethylene molecules appeared at the 24 fold position (0.2773, 0.3574, 0.3574) with a peak height of 1.3(2) $e\text{Å}^{-3}$. The occupancy number of C per unit cell refined to $C=13.1(8)$. The carbon atoms are associated with Ag^+ ions at Ag(1) and Zn^{2+} ions at Zn(2). Therefore, refinement of about 11.2 carbon atoms per unit cell at this position, constrained to be no more than twice the number of 2.8 Ag^+ ions and 2.8 Zn^{2+} ions, converged readily, but gave a large isotropic thermal parameter (10(1) Å²). Hence a trial refinement with carbon atom at a general position (x, y, z), similar to the ethylene sorption complex of $Co_4Na_4A^{17}$, converged to a lower isotropic thermal parameter (7(1) Å²) for carbon. This model lowered the error indices to $R_1=0.053$ and $R_2=0.050$. Anisotropic thermal parameters for all species except ethylene molecules were employed in the refinement (see Table 1). In the final cycle of least-squares refinement, all shifts in atomic parameters were less than 0.3% of their corresponding standard deviations. The final difference Fourier function was featureless except one at (0.0, 0.0, 0.0) with peak height of 2.7(10) $e\text{Å}^{-3}$.

The full-matrix least-squares program used in all structure determinations minimized $\sum(F_o -$

Table 1. Positional, thermal^a and occupancy parameters of dehydrated $\text{Ag}_2\text{Zn}_{16}\text{S}_8\text{A}$ and of its ethylene sorption complex(a) $\text{Ag}_2\text{Zn}_{16}\text{S}_8\text{A}$

Atom	Wyc. Pos.	x	y	z	β_{11}^b	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy	
											varied	fixed
(Si, Al)	24(k)	0	1830(3)	3664(2)	23(1)	16(2)	14(1)	0	0	-1(3)		1.0 ^c
O(1)	12(h)	0	1931(3)	5000	70(10)	43(8)	39(8)	0	0	0		1.0
O(2)	12(i)	0	2994(5)	2994(5)	35(7)	21(4)	21(4)	0	0	20(10)		1.0
O(3)	24(m)	1123(4)	1123(4)	3205(5)	57(3)	57(3)	28(5)	77(9)	-16(8)	-16(8)		1.0
Ag(1)	8(g)	1852(2)	1852(2)	1852(2)	33(1)	33(1)	33(1)	37(3)	37(3)	37(3)	0.339(3)	0.350
Zn(1)	8(g)	1560(6)	1560(6)	1560(6)	54(3)	54(3)	54(3)	44(8)	44(8)	44(8)	0.263(5)	0.250
Zn(2)	8(g)	2020(3)	2020(3)	2020(3)	26(2)	26(2)	26(2)	17(5)	17(5)	17(5)	0.329(4)	0.325

(b) $\text{Ag}_2\text{Zn}_{16}\text{S}_8\text{A} \cdot 5.6\text{C}_2\text{H}_4$

Atom	Wyc. Pos.	x	y	z	β_{11}^b	B_{300}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy	
												varied	fixed
(Si, Al)	24(k)	0	1822(2)	3662(2)	19(1)	19(1)	14(1)	13(1)	0	0	5(2)		1.0 ^c
O(1)	12(h)	0	1941(9)	5000	83(8)	83(8)	49(7)	30(6)	0	0	0		1.0
O(2)	12(i)	0	3024(5)	3024(5)	31(5)	31(5)	23(3)	23(3)	0	0	18(19)		1.0
O(3)	24(m)	1142(4)	1142(5)	3207(5)	41(3)	41(3)	41(3)	44(4)	39(7)	-29(6)	-29(6)		1.0
Ag(1)	8(g)	2271(2)	2271(2)	2271(2)	46(1)	46(1)	46(1)	46(1)	32(3)	32(3)	32(3)	0.355(6)	0.350
Zn(1)	8(g)	1580(6)	1580(6)	1580(6)	57(3)	57(3)	57(3)	66(7)	66(7)	66(7)	66(7)	0.224(9)	0.225
Zn(2)	8(g)	2025(2)	2025(2)	2025(2)	20(1)	20(1)	20(1)	20(1)	12(3)	12(3)	12(3)	0.375(9)	0.350
C	48(n)	2870(30)	3306(30)	3730(30)	7(1) ^d							0.273(17)	0.233

^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 = $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. Rms displacements can be calculated from B_i values by using the formula, $U_i = 0.225a(\beta_{ii})^{1/2}$, where $a = 12.137(2)$ Å for $\text{Ag}_2\text{Zn}_{16}\text{S}_8\text{A}$ and $a = 12.106(2)$ Å for $\text{Ag}_2\text{Zn}_{16}\text{S}_8\text{A} \cdot 5.6\text{C}_2\text{H}_4$. ^cOccupancy for (Si) = 1/2; occupancy for (Al) = 1/2. ^dIsotropic thermal parameter in units of Å².

$|F_c|^2$; the weight (w) of an observation was the reciprocal square of $\sigma(F_o)$, its standard deviation. Atomic scattering factors¹⁸ for (Si, Al)¹⁷⁵⁺ (the average of Si⁰, Si⁴⁺, Al⁰, and Al³⁺), O⁻, Zn²⁺, Ag⁺ and C (valence) were used. All scattering factors were modified to account for the anomalous dispersion correction^{19,20}.

DISCUSSION

Dehydrated Ag_{2.8}Zn_{4.6}-A. 2.8 Ag⁺ ions at Ag(1) are located on the threefold axes of the unit cell (see Table 1). These Ag⁺ are coordinated to three O(3) framework oxygens at 2.065(6) Å. The O(3)-Ag(1)-O(3) angle of 119.9(1)° indicates that Ag(1) has achieved trigonal-planar coordination (see

Table 2. Selected interatomic distances (Å) and Angles (deg)

Interatom	Ag _{2.8} Zn _{4.6} -A	Ag _{2.8} Zn _{4.6} -A·5.6C ₂ H ₄
(Si, Al)-O(1)	1.626(2)	1.626(2)
(Si, Al)-O(2)	1.630(4)	1.648(4)
(Si, Al)-O(3)	1.704(4)	1.701(3)
Ag(1)-O(3)	2.065(6)	2.240(4)
Zn(1)-O(3)	2.133(6)	2.108(6)
Zn(2)-O(3)	2.106(5)	2.082(5)
Ag(1)-C		2.29(4)
Zn(2)-C		2.78(4)
C-C		1.47(5)
O(1)-(Si, Al)-O(2)	115.6(4)	112.8(4)
O(1)-(Si, Al)-O(3)	111.4(3)	111.4(3)
O(2)-(Si, Al)-O(3)	105.8(2)	106.0(2)
O(3)-(Si, Al)-O(3)	106.3(3)	108.8(2)
(Si, Al)-O(1)-(Si, Al)	171.3(8)	169.8(7)
(Si, Al)-O(2)-(Si, Al)	149.9(3)	145.9(3)
(Si, Al)-O(3)-(Si, Al)	134.2(4)	133.1(3)
O(3)-Ag(1)-O(3)	119.9(1)	104.2(1)
O(3)-Zn(1)-O(3)	113.8(2)	114.0(2)
O(3)-Zn(2)-O(3)	116.0(1)	116.3(1)
O(3)-Ag(1)-C		97.7(9)
O(3)-Zn(2)-C		87.9(7)
C-Ag(1)-C		32(1)
C-Zn(2)-C		27(2)
C-C-Ag(1)		71(2)
C-C-Zn(2)		75(2)

*Numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding value.

Table 2). Ag⁺ ions lie almost the center of (111) plane of three O(3) atoms.

2.0 Zn²⁺ ions at Zn(1) are located on the threefold axes and lie relatively far inside the sodalite cavity from the (111) plane at O(3) with Zn(1)-O(3) distances of 2.144(6) Å.

2.6 Zn²⁺ ions at Zn(2) are also on the threefold axes of unit cell and associate with 6-rings. They are recessed 0.426(2) Å into the large cavity from the (111) plane at O(3) (see Table 3). Zn(2) is 2.106(5) Å to three O(3) atoms, close to the sum of the conventional ionic radii of Zn²⁺ and O²⁻, 2.06 Å²¹.

In this structure, both Zn²⁺ ions and Ag⁺ ions occupy only 6-ring sites and the 8-ring (and 4-ring) sites are empty. This result shows that Ag⁺ ion and Zn²⁺ ions which have relatively small ionic radii (ionic radius of Ag⁺=1.26 Å and that of Zn²⁺=0.74 Å)¹⁹ prefer the 6-ring sites to the 8-ring sites.

A plausible arrangement of the large cavity of the Ag_{2.8}Zn_{4.6}-A is presented in Fig. 1. To minimize

Table 3. Deviation of atoms(Å) from the (111) plane at O(3)

Atom	Ag _{2.8} Zn _{4.6} -A	Ag _{2.8} Zn _{4.6} -A·5.6C ₂ H ₄
O(2)	0.375(4)	0.389(3)
Ag(1)	0.073(2)	0.922(2)
Zn(1)	-0.541(4)	-0.527(4)
Zn(2)	0.426(2)	0.408(2)
C		3.087(3)

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

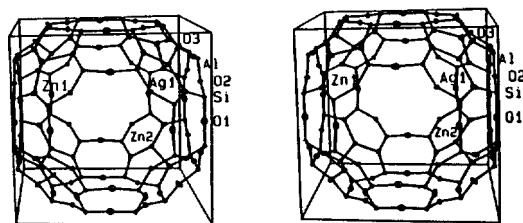


Fig. 1. A stereoview of a large cavity of dehydrated Ag_{2.8}Zn_{4.6}-A. Two Ag⁺ ions at Ag(1), two Zn²⁺ ions at Zn(1), and three Zn²⁺ ions at Zn(2) are shown. About 60% of the large cavities may have this arrangement. Ellipsoids of 25% probability are used.

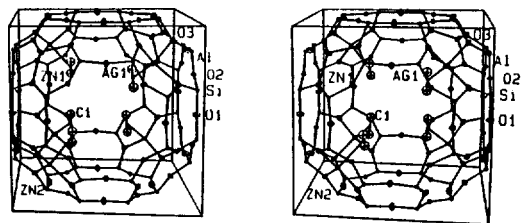


Fig. 2. A stereoview of a large cavity of dehydrated $\text{Ag}_{2.8}\text{Zn}_{4.6}\text{-A}\cdot 5.6\text{C}_2\text{H}_4$. 2 Ag^+ ions at Ag(1), 2 Zn^{2+} ions at Zn(1), 3 Zn^{2+} ions at Zn(2), and 5 C_2H_4 molecules at C are shown. About 60% of the large cavities may have this arrangement. Ellipsoids of 25% probability are used.

electrostatic repulsions, the Zn^{2+} ions at Zn(1) are placed triangular fashion, and the Ag^+ ions and Zn(1) ions are filled the remained threefold axis equipoints of the unit cell.

The fractional occupancies observed at Ag(1) and Zn(2) indicate the existence of at least 2 types of unit cells. About 60% of unit cells may have 2 Ag^+ ions at Ag(1), 2 Zn^{2+} ions at Zn(1), and 3 Zn^{2+} ions at Zn(2). Remaining 40% may consist of 4 Ag^+ ions at Ag(1), 2 Zn^{2+} ions at Zn(1), and 2 Zn^{2+} (see Fig. 1).

$\text{Ag}_{2.8}\text{Zn}_{4.6}\text{-A}\cdot 5.6\text{C}_2\text{H}_4$. A comparison of the structure of $\text{Ag}_{2.8}\text{Zn}_{4.6}\text{-A}\cdot 5.6\text{C}_2\text{H}_4$ with that of the dehydrated $\text{Ag}_{2.8}\text{Zn}_{4.6}\text{-A}$, reveals some changes of bond lengths and distances (see Table 1).

Each ethylene molecule forms a lateral π complex (see Fig. 2) with a 6-ring Ag^+ ion. To bind one molecule of ethylene, each Ag^+ ion of the dehydrated $\text{Ag}_{2.8}\text{Zn}_{4.6}\text{-A}$ moves significant distance (ca. 0.85 Å, see Table 2) from its triad of O(3) atoms, further into the large cavity. Accordingly, the length of the Ag(1)-O(3) bond has increased from 2.065(6) Å in the dehydrated structure to 2.240(4) Å (see Table 2) in ethylene sorption structure. The three equivalent O(3)-Ag(1)-O(3) angles have decreased correspondingly from the trigonal planar value of 119.9(1)° in dehydrated $\text{Ag}_{2.8}\text{Zn}_{4.6}\text{-A}$ to near tetrahedral value of 104.2(1)° after the sorption of ethylene (see Table 2). With the exception of an decrease of 4° in the (Si, Al)-O(2)-(Si, Al) angle, no significant change in framework structure has resulted from the sorption of ethylene.

The Ag(1)-C bond length of the $\text{Ag}_{2.8}\text{Zn}_{4.6}\text{-A}\cdot 5.6\text{C}_2\text{H}_4$, 2.29(4) Å, indicates that the ethylene is firmly held by the Ag^+ ion at Ag(1). 2.8 Ag^+ ions are recessed 0.922(2) Å from (111) plane of three 6-ring oxygens into the large cavity (see Table 3).

The Zn^{2+} ions occupy two different threefold axis positions of the unit cell. 2.8 Zn^{2+} ions are recessed 0.408(2) Å from (111) plane of the 6-ring oxygens (see Table 3).

The positions of Zn^{2+} ions at Zn(2) are almost unchanged: Zn(2)-O(3) distances are 2.106(5) Å in the dehydrated structure and 2.082(5) Å in its ethylene sorption complex, respectively. And no changes in the angles formed at Zn^{2+} ions are observed (see Table 2). Although Zn(2)-C distance, 2.78(4) Å is relatively long, the occupancies of ethylene revealed that each Zn^{2+} was weakly bound to an ethylene. The positions of ethylene molecules which were bound to Zn^{2+} ions must be somewhat different from those bound to Ag^+ ions. However, this could not be resolved crystallographically.

The bonding between transition metals and alkenes is usually described in terms of the Chatt-Dewar model²². An initial σ bond is formed between the filled π orbital of the alkene and an empty σ -acceptor orbital of the metal (for example, 5s orbital of Ag^+ ion and 4s orbital of Zn^{2+} ion). Accumulated negative charge on the metal then is "back-donated" by d π orbitals of the metal to a π -acceptor orbital of the alkene. This effect strengthens not only the preliminary σ bond but also synergically reinforces the π bond as well. Because the π -acceptor orbital of the alkene is antibonding, the C=C bond order may be diminished somewhat by back-donation, and such an effect may be indicated by a lengthening of the C=C bond. The long ethylene double bond, the C=C distance of 1.47(5) Å may be reflect this back-donation. The difference between Zn^{2+} and Ag^+ ions in their ability to back-donate 3d and 4d electrons, respectively, to the π^* orbitals of ethylene lies in their difference in ionic radii. Divalent Zn^{2+} ion, has an ionic radius of 0.74 Å, compared to 1.26 Å for the monovalent Ag^+ ion. This suggests that the filled 3d orbitals of Zn^{2+} ion do not reach sufficiently far out in space to

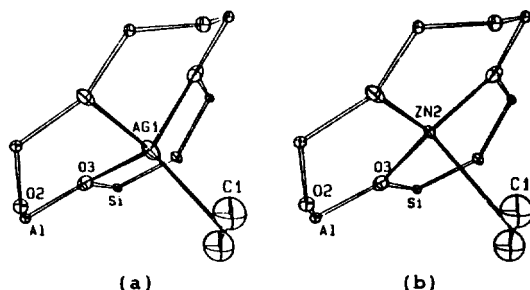


Fig. 3. The coordination environments of the Ag(I) and Zn(II) ions. An $\text{Ag}(\text{C}_2\text{H}_4)^+$ complex (a) and a $\text{Zn}(\text{C}_2\text{H}_4)^{2+}$ complex (b) in large cavity. The hydrogen atoms whose position were not determined are not shown. Ellipsoids of 25% probability are used.

overlap effectively, as $4d$ orbitals of Ag^+ ion do. The Ag^+-C distance, $2.29(4) \text{ \AA}$ is much shorter than the $\text{Zn}^{2+}-\text{C}$ distance, $2.78(4) \text{ \AA}$. Therefore, $\text{Zn}^{2+}-\text{C}_2\text{H}_4$ complexes in zeolite A have much weaker interaction than $\text{Ag}^+-\text{C}_2\text{H}_4$ complexes.

The Zn^{2+} ions at Zn(1) have no distinct change upon ethylene sorption (see Table 1 and 2). The distance between the Zn(1) ion and ethylene is 3.69 \AA , too long to be an interaction. Although the uncertainties in the carbon position are large and the determination of the $\text{C}=\text{C}$ distance is poor, it is still clear that the ethylene molecules make so significant approaches to the zeolite framework. The closet $\text{C}-\text{O}$ approach is 3.41 \AA to an O(3) ion (see Fig. 3). The hydrogen atoms would therefore also be too far from the nearest oxide ions to interact with them.

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