

Crystal Structures of Dehydrated Ag^+ and Ca^{2+} Exchanged Zeolite A, $\text{Ag}_{3.3}\text{Ca}_{4.35}\text{-A}$ and of Its Ethylene Sorption Complex

Se Bok Jang, Jong Yul Park, Yunghee Oh Kim, and Yang Kim*

Department of Chemistry, Pusan National University, Pusan 609-735

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Two crystal structures of dehydrated $\text{Ag}_{3.3}\text{Ca}_{4.35}\text{-A}$ ($a=12.256(2)$ Å) and of its ethylene sorption complex ($a=12.259(2)$ Å) have been determined by single-crystal X-ray diffraction techniques in the cubic space group $Pm\bar{3}m$ at $21(1)^\circ\text{C}$. Both crystals were dehydrated at 360°C and 2×10^{-6} Torr for 2 days and one crystal was treated with 200 Torr of ethylene at $24(2)^\circ\text{C}$. The structures were refined to final error indices, $R_1=0.065$ and $R_2=0.088$ with 202 reflections and $R_1=0.049$ and $R_2=0.044$ with 259 reflections, respectively, for which $I > 3\sigma(I)$. In these structures, all Ag^+ and Ca^{2+} ions are located on two and three different threefold axes associated with 6-ring oxygens, respectively. In $\text{Ag}_{3.3}\text{Ca}_{4.35}\text{-A} \cdot 6.65 \text{C}_2\text{H}_4$, 3.3 Ag^+ and 3.35 Ca^{2+} ions are recessed 1.09 Å and 0.21 Å, respectively, into the large cavity from the (111) plane at O(3). Each Ag^+ and Ca^{2+} ion in the large cavity forms a complex with one C_2H_4 molecule. Distances between Ca^{2+} ions and ethylene molecules are longer than those between Ag^+ ions and ethylene molecules.

Introduction

Zeolites are high-capacity and highly selective sorbents due to the presence of channels in their structures. Generally sorbates are selected on the basis of size. The structural informations of the various sorbates in the inner surface of the zeolite A have been obtained by the very powerful crystallographic method.

Several hydrocarbon sorption structures of transition metal ion exchanged zeolite A have been studied. In the structures of dehydrated $\text{Co}_4\text{Na}_4\text{-A}$ ¹ and $\text{Mn}_4\text{Na}_4\text{-A}$,² the transition metal ions adopt positions close to the anionic zeolite framework where they achieve near-trigonal planar coordinations close to the anionic zeolite framework. Upon treating dehydrated $\text{Co}_4\text{Na}_4\text{-A}$ and $\text{Mn}_4\text{Na}_4\text{-A}$ with ethylene and acetylene molecules,³⁻⁵ respectively, four ethylene and/or acetylene molecules per unit cell are sorbed. Each of four transition metal ions lies on threefold axes in the large cavity of unit cell, close to three equivalent trigonally arranged zeolite oxygen atoms and symmetrically close to both carbon atoms of C_2H_4 molecules and/or C_2H_2 molecules. In the crystal structure of an ethylene sorption complex, partially decomposed and fully Ag^+ -exchanged zeolite A,⁶ 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 located 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 ($\text{C}-\text{C}=1.19(12)$ Å).

Recently, the crystal structure of ethylene sorption complexes of dehydrated $\text{Ag}_{2.8}\text{Zn}_{4.6}\text{-A}$, has been determined.⁷ In this structure, 2.8 Ag^+ ions and 2.8 Zn^{2+} ions are recessed 0.922(2) Å and 0.408(2) Å, respectively from (111) plane of three 6-ring oxygens into the large cavity where each forms a complex with an ethylene molecule ($\text{Ag}^+-\text{C}=2.29(5)$ Å and $\text{Zn}^{2+}-\text{C}=2.78(4)$ Å).

In the crystal structures of dehydrated Ca^{2+} -exchanged zeolite A treated with ethylene and acetylene,⁸ respectively, Ca^{2+} ions are distributed over two distinguished threefold axes of the unit cell. Four of these extend somewhat into

the large cavity where each is coordinated to three framework oxide ions and ethylene molecule and/or acetylene molecule. The distances between Ca^{2+} ion and carbon atom are 2.87(7) Å in ethylene sorption structure and 2.95 (7) Å in acetylene sorption structure. These chemical bondings are relatively weak.

This study was done to learn the selective positions of Ag^+ and Ca^{2+} ions within zeolite A and to investigate the geometry of the sorbed ethylene molecules which may form complexes with Ag^+ ions and/or Ca^{2+} ions.

Experimental

Crystals of zeolite 4A were prepared by modification of Charnell's method,⁹ including a second crystallization using seed crystals. Each of two single crystals about 85 μm on edge was selected and lodged in a fine capillary.

Two crystals of approximate unit cell composition of $\text{Ag}_{3.3}\text{Ca}_{4.35}\text{Si}_{12}\text{Al}_{12}\text{O}_{46} \cdot x\text{H}_2\text{O}$ were prepared by flow methods using exchange solutions in which molar ratios of AgNO_3 and $\text{Ca}(\text{NO}_3)_2$ were 1 to 200, with a total concentration of 0.05 M. 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 at $21(1)^\circ\text{C}$. Each crystal was placed in a finely drawn Pyrex capillary, attached to a vacuum system and cautiously dehydrated by gradually increasing its temperature (ca. $25^\circ/\text{hr}$) to 360°C at a constant pressure of 2×10^{-6} Torr. Finally, system was maintained at the state for 48 hrs.

To prepare the ethylene complex, the crystal was treated with 200 Torr of zeolitically dried ethylene for 1 hr at $24(1)^\circ\text{C}$. Under these conditions, the crystal was removed in its capillary from the vacuum system by torch. Microscopic examination showed that both crystals were remained colorless.

X-ray Data Collection

The cubic space group $Pm\bar{3}m$ (no systematic absences) was used instead of $Fm\bar{3}c$ throughout this work for reasons discussed previously.^{10,11} Diffraction data were collected with an automated Enraf-Nonius four-circle computer controlled

Table 1. Positional,^a Thermal, and Occupancy Parameters
(a) Crystal 1. Dehydrated $\text{Ag}_{3.3}\text{Ca}_{4.35}\text{-A}$

Atom	Wyckoff position	x	y	z	β_{11}^b	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy ^c	
											Varied	Fixed
(Si, Al)	24(k)	0	1829(5)	3702(4)	29(3)	20(3)	23(3)	0	0	15(6)	24.0 ^d	
O(1)	12(h)	0	2160(20)	5000	70(20)	60(20)	40(20)	0	0	0	12.0	
O(2)	12(i)	0	2870(10)	2870(10)	100(20)	36(8)	36(8)	0	0	70(20)	12.0	
O(3)	24(m)	1104(8)	1104(8)	3340(10)	48(6)	48(6)	60(20)	50(10)	-0(20)	-0(20)	24.0	
Ag(1)	8(g)	1950(4)	1950(4)	1950(4)	65(4)	114(5)	65(2)	65(2)	114(5)	114(5)	3.27(3)	3.3
Ca(1)	8(g)	1630(20)	1630(20)	1630(20)	279(8)	279(8)	279(8)	480(20)	480(20)	480(2)	4.43(8)	4.35

(b) Crystal 2. Ethylene Sorption Complexes of $\text{Ag}_{3.3}\text{Ca}_{4.35}\text{-A}$

Atom	Wyckoff position	x	y	z	β_{11}^b	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy ^c	
											Varied	Fixed
(Si, Al)	24(k)	0	1823(2)	3703(2)	24(1)	17(1)	10(1)	0	0	7(3)	24.0 ^d	
O(1)	12(h)	0	2141(6)	5000	51(7)	34(6)	28(6)	0	0	0	12.0	
O(2)	12(i)	0	2890(5)	2890(5)	93(9)	29(4)	29(4)	0	0	40(10)	12.0	
O(3)	24(m)	1120(4)	1120(4)	3357(4)	47(3)	47(3)	32(4)	28(9)	6(6)	6(6)	24.0	
Ag(1)	8(g)	2381(2)	2381(2)	2381(2)	43(9)	43(9)	43(9)	24(3)	24(3)	24(3)	3.27(2)	3.3
Ca(1)	8(g)	1965(4)	1965(4)	1965(4)	36(3)	36(3)	36(3)	5(6)	5(6)	5(6)	3.43(6)	3.35
Ca(2)	8(g)	1530(20)	1530(20)	1530(20)	62(8)	62(8)	62(8)	120(20)	120(20)	120(20)	1.01(6)	1.0
C(1)	24(m)	3120(10)	3120(10)	3850(20)	330(30)	330(30)	140(30)	-340(50)	-120(30)	-120(30)	15.10(9)	13.3

^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 = $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. ^cOccupancy factors given as the number of atoms or ions per unit cell. ^dOccupancy for (Si) = 12; occupancy for (Al) = 12.

CAD-4 diffractometer equipped with a pulse-height analyzer and a graphite monochromator, using Mo K α radiation (K α_1 , $\lambda = 0.70930$ Å, K α_2 , $\lambda = 0.71359$ Å). In each case, the unit cell constants at 21(1)°C determined by least squares refinement of 25 intense reflections for which $18^\circ < 2\theta < 25^\circ$ are $a = 12.256(2)$ Å for $\text{Ag}_{3.3}\text{Ca}_{4.35}\text{-A}$ and $a = 12.259(2)$ Å for $\text{Ag}_{3.3}\text{Ca}_{4.35}\text{-A} \cdot 6.65\text{C}_2\text{H}_4$, respectively.

For each crystal, reflections from two intensity-equivalent regions of reciprocal space (hkl , $h \leq k \leq l$ and lkh , $l \leq h \leq k$) were examined. The intensities were measured using ω - 2θ scan technique over a scan width of $(0.80 + 0.344 \tan \theta)^\circ$ in ω . The data were collected using the variable scan speeds. Most reflections were observed at slow scan speeds, ranging between 0.24° and $0.39^\circ \text{ deg min}^{-1}$ in ω . The intensities of three reflections in diverse regions of reciprocal space were recorded after every three hours to monitor crystal x-ray source stability. Only small, random fluctuations of these check reflections were noted during the course of data collections. For each regions of reciprocal space, the intensities of all lattice points for which $2\theta < 70^\circ$ were recorded.

The intensities were corrected for Lorentz and polarization effects; the reduced intensities were merged and the resultant estimated standard deviations were assigned to each average reflection by the computer programs, PAINT and WEIGHT.¹²

An absorption correction ($\mu R = 0.066$, $\rho_{\text{cal}} = 1.767 \text{ g/cm}^3$ and $F(000) = 944$ for $\text{Ag}_{3.3}\text{Ca}_{4.35}\text{-A}$, and $\mu R = 0.073$, $\rho_{\text{cal}} = 1.935 \text{ g/cm}^3$ and $F(000) = 1050$ for $\text{Ag}_{3.3}\text{Ca}_{4.35}\text{-A} \cdot 6.65\text{C}_2\text{H}_4$) was judged to be negligible and was not applied.¹³ All unique reflections for which $2\theta < 70^\circ$ for crystals were examined by counter me-

thods. Only those of which $I > 3\sigma(I)$ were used for structure solution and refinement. These amounted to 202 of the 874 reflections examined for the $\text{Ag}_{3.3}\text{Ca}_{4.35}\text{-A}$, and 259 of the 877 reflections for the $\text{Ag}_{3.3}\text{Ca}_{4.35}\text{-A} \cdot 6.65\text{C}_2\text{H}_4$, respectively.

Structure Determination

Dehydrated $\text{Ag}_{3.3}\text{Ca}_{4.35}\text{-A}$. Full-matrix least-squares refinement was initiated using the atomic parameters of the framework atoms converged [(Si, Al), O(1), O(2), and O(3)] in the structure of dehydrated $\text{Ag}_2\text{Ca}_5\text{-A}$.¹⁴ Anisotropic refinement of the framework atoms converged to an R_1 index, $(\Sigma |F_o - |F_c|| / \Sigma F_o)$ of 0.361 and a weighted R_2 index, $(\Sigma w(F_o - |F_c|)^2 / \Sigma w F_o^2)^{1/2}$ of 0.495.

The initial difference Fourier function revealed one large peak at (0.193, 0.193, 0.193) of height $9.03(20) \text{ e} \text{ \AA}^{-3}$. Inclusion of this peak as Ag(1) lowered the error indices of $R_1 = 0.172$ and $R_2 = 0.177$ (see Table 1).

A difference Fourier function revealed a peak at (0.166, 0.166, 0.166) with a height of $3.76(17) \text{ e} \text{ \AA}^{-3}$. Simultaneous positional, thermal, and occupancy refinement including this positions as Ca(1) converged to $R_1 = 0.106$ and $R_2 = 0.084$.

It is not so difficult to distinguish Ag^+ from Ca^{2+} ions for several reasons. First, the atomic scattering factors are different, 46 e^- for Ag^+ vs. 18 e^- for Ca^{2+} . Second, the ionic radii are different, $\text{Ag}^+ = 1.26$ Å and $\text{Ca}^{2+} = 0.99$ Å.¹⁵

The occupancy numbers of Ag^+ and Ca^{2+} ions per unit cell were refined to Ag(1) = 3.27(3), and Ca(1) = 4.43(8). These were fixed at Ag(1) = 3.3, Ca(1) = 4.35, respectively because the cationic charge should not be exceeded +12 per $Pm\bar{3}m$

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

Interatom	Ag _{3.3} Ca _{4.35} -A	Ag _{3.3} Ca _{4.35} -A·6.65C ₇ H ₄
(Si, Al)-O(1)	1.642(7)	1.637(3)
(Si, Al)-O(2)	1.63(1)	1.644(4)
(Si, Al)-O(3)	1.678(7)	1.676(3)
Ag(1)-O(3)	2.26(1)	2.492(4)
Ca(1)-O(3)	2.29(1)	2.249(5)
Ca(2)-O(3)		2.349(7)
Ag(1)-C(1)		2.21(2)
Ca(1)-C(1)		3.06(2)
C(1)-C(1)		1.27(3)
O(1)-(Si, Al)-O(2)	114.5(8)	113.5(3)
O(1)-(Si, Al)-O(3)	112.7(6)	111.6(2)
O(2)-(Si, Al)-O(3)	104.4(5)	104.8(2)
O(3)-(Si, Al)-O(3)	107.6(5)	110.1(2)
(Si, Al)-O(1)-(Si, Al)	152(1)	152.4(5)
(Si, Al)-O(2)-(Si, Al)	167.6(7)	164.6(3)
(Si, Al)-O(3)-(Si, Al)	141.8(8)	141.2(3)
O(3)-Ag(1)-O(3)	119.1(3)	102.2(1)
O(3)-Ca(1)-O(3)	115.9(7)	119.1(1)
O(3)-Ca(2)-O(3)		111.4(3)
O(3)-Ag(1)-C(1)		96.6(5)
O(3)-Ca(1)-C(1)		81.5(5)
C(1)-Ag(1)-C(1)		33.5(7)
C(1)-Ca(1)-C(1)		24.0(5)
Ag(1)-C(1)-C(1)		73(1)
Ca(1)-C(1)-C(1)		78(1)

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

unit cell.

The final R values were $R_1=0.065$ and $R_2=0.088$. The difference function was featureless except $1.6(8) e\text{\AA}^{-3}$ at (0.0, 0.0, 0.0). This peak was not refined at the least-squares refinement.

Ag_{3.3}Ca_{4.35}-A·6.65C₇H₄. Initial full-matrix least-squares refinement was initiated by using the atomic parameters of framework atoms from the previous crystal of Ag_{3.3}Ca_{4.35}-A. Anisotropic refinement of the framework atoms converged to $R_1=0.409$ and $R_2=0.479$, respectively.

A difference electron density function revealed one large peak at (0.220, 0.220, 0.220) with height of $13.12(25) e\text{\AA}^{-3}$. This peak was stable at least-squares refinement and converged to $R_1=0.194$ and $R_2=0.185$.

A subsequent difference Fourier function revealed two large threefold axis peaks at (0.193, 0.193, 0.193) and (0.150, 0.150, 0.150) with heights of $4.58(28) e\text{\AA}^{-3}$ and $2.18(30) e\text{\AA}^{-3}$, respectively. This peak was stable in the least-squares refinement. Anisotropic refinement including these Ca²⁺ ions at Ca(2) and Ca(3) positions converged to $R_1=0.072$ and $R_2=0.098$.

A successive difference Fourier map revealed the carbon atoms of ethylene molecules at the 24-fold position (0.30, 0.30, 0.38). This corresponds closely to the final result, in which approximately 13.3 carbon atoms are found very near this position. The occupancy numbers of carbon atoms indi-

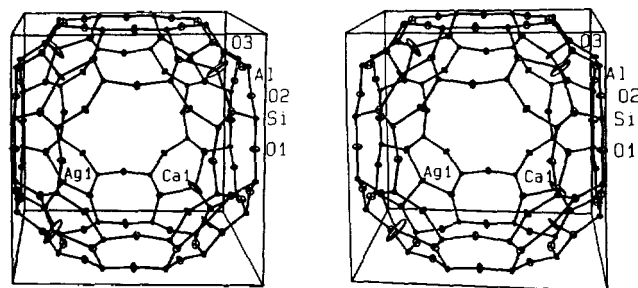


Figure 1. (a) A stereoview of a large cavity of dehydrated Ag_{3.3}Ca_{4.35}-A. Four Ag⁺ ions at Ag(1) and four Ca²⁺ ions at Ca(1) are shown. About 65% of the unit cells may have this arrangement.

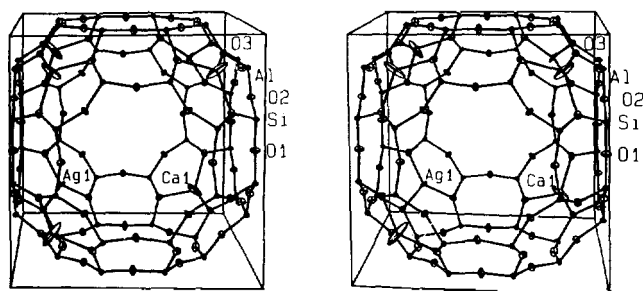


Figure 2. (b) A stereoview of a large cavity of dehydrated Ag_{3.3}Ca_{4.35}-A. Two Ag⁺ ions at Ag(1) and five Ca²⁺ ions at Ca(1) are shown. Atoms and ions are placed within their equipoints of partial occupancy in a chemically plausible manner. About 35% of the unit cells may have this arrangement.

cate that the carbon atoms were associated with Ag⁺ ions at Ag(1) and Ca²⁺ ions at Ca(1). Therefore, the refinement of about 6.65 carbon atoms per unit cell at this position, constrained to be no more than twice the number of Ag⁺ ions and Ca²⁺ ions at Ca(1), converged readily. Refinement of a model, with all carbon atoms treated anisotropically, converged to $R_1=0.049$ and $R_2=0.044$ (see Table 1).

For all structures, 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 $\sigma(F_o)$, its standard deviation. Atomic scattering factors^{16,17} for C⁰ (valence), Ag⁺, Ca²⁺, 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 the anomalous dispersion correction.¹⁸ The final structural parameters and selected interatomic distances and angles are presented in Table 1 and 2, respectively.

Discussion

In the crystal structure of dehydrated Ag_{3.3}Ca_{4.35}-A, all Ag⁺ and Ca²⁺ ions are found on two distinguished three fold axes (see Table 1 and Figure 1, 2). About 3.3 Ag⁺ ions at Ag(1) extends 0.217(3) Å into the large cavity from the (111) plane at O(3) and are coordinated to three O(3) oxygens at 2.26(1) Å in a slightly distorted trigonal planar arrangement. About 4.35 Ca²⁺ ions at Ca(1) are recessed 0.473(16) Å into the sodalite unit from the O(3) planes of the 6-ring.

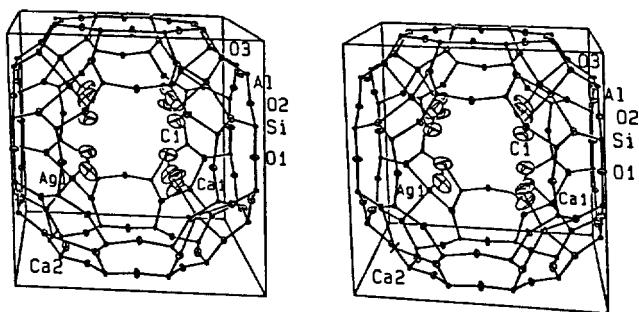


Figure 3. A stereoview of a large cavity of dehydrated $\text{Ag}_{3.3}\text{Ca}_{4.35}\text{A} \cdot 6.65\text{C}_2\text{H}_4$. 4 Ag^+ ions at Ag(1), 3 Ca^{2+} ion at Ca(1), 1 Ca^{2+} ion at Ca(2), and 7 C_2H_4 molecules at C(1) are shown. Atoms and ions are placed within their equipoints of partial occupancy in a chemically plausible manner. About 65% of the large cavities may have this arrangement. Ellipsoids of 20% probability are used.

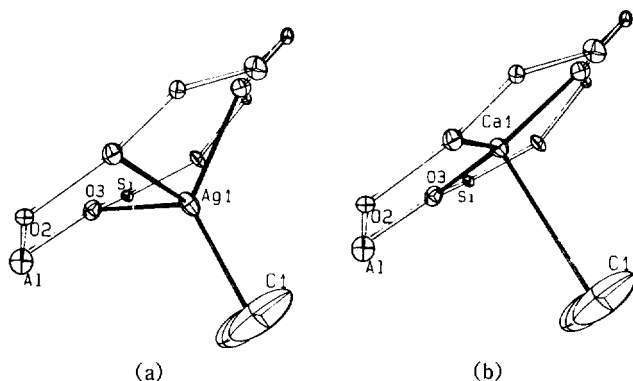


Figure 4. The coordination environments of the Ag^+ and Ca^{2+} ions. An $\text{Ag}(\text{C}_2\text{H}_4)^+$ complex (a) and a $\text{Ca}(\text{C}_2\text{H}_4)^{2+}$ complex (b) in large cavity. The hydrogen atoms whose position were not determined are not shown. Ellipsoids of 20% probability are used.

Each of these Ca^{2+} ions at Ca(1) is coordinated to three O(3) framework oxygens at 2.29(1) Å.

The fractional occupancies observed at Ag(1) and Ca(1) of dehydrated $\text{Ag}_{3.3}\text{Ca}_{4.35}\text{A}$ indicate the existence of approximately two types of unit cell. For example, about 65% of the unit cells may have 4 Ag^+ ions at Ag(1) and 4 Ca^{2+} ions at Ca(1), and the remaining 35% would have 2 Ag^+ ions at Ag(1) and 5 Ca^{2+} ions at Ca(1).

The fractional occupancies observed at Ag^+ ions and Ca^{2+} ions in the structure of $\text{Ag}_{3.3}\text{Ca}_{4.35}\text{A} \cdot 6.65\text{C}_2\text{H}_4$ indicate that about 65% of the unit cells may consist of 4 Ag^+ ions at Ag(1), 3 Ca^{2+} ions at Ca(1), 1 Ca^{2+} ion at Ca(2), and 7 ethylene molecules (Figure 3). About 35% of the unit cells may have 2 Ag^+ ions at Ag(1), 4 Ca^{2+} ions Ca(1), 1 Ca^{2+} ion at Ca(2), and 6 ethylene molecules.

To coordinate to ethylene, Ag^+ ions at Ag(1) moved significant distance (ca. 0.88 Å) into the large cavity (see Figures 1, 2 and 4) and away from their triads of three O(3) oxide ions, to more tetrahedral coordination site (considering ethylene to be monodentate). The lengths of the Ag(1)-O(3) bonds have increased from 2.26(1) Å in the dehydrated structure of 2.49 Å in ethylene sorption structure as the coordination

Table 3. Deviation of atom (Å) from the (111) Plane at O(3)

Atom	$\text{Ag}_{3.3}\text{Ca}_{4.35}\text{A}$	$\text{Ag}_{3.3}\text{Ca}_{4.35}\text{A} \cdot 6.65\text{C}_2\text{H}_4$
O(2)	0.130(8)	0.129(4)
Ag(1)	0.211(3)	1.094(1)
Ca(1)	-0.473(4)	0.211(3)
Ca(2)		-0.708(12)
C(1)		3.181(20)

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

of Ag^+ has changed from trigonal to near tetrahedral, with an increase of one in coordination number. The O(3)-Ag(1)-O(3) angle has decreased accordingly from a nearly planar value, 119.1(3)° in dehydrated structure to 102.2(1)°, after ethylene complexation (see Table 2).

The Ca^{2+} ions at Ca(1) in ethylene sorption structure occupy threefold axis position near 6-ring, recessed 0.08 Å into the large cavity from the (111) plane at O(3). These cations approach to three O(3) framework oxygens at distance of 2.25(1) Å.

Each ethylene molecules interact either with a 6-ring Ag^+ ion or a 6-ring Ca^{2+} ion at Ca(1). The bonding distance between Ag^+ ion and carbon atom is 2.21(2) Å and that between a Ca^{2+} ion and carbon atom is 3.06(2) Å. The Ag^+ ion to carbon distance in the ethylene sorption complex of Ag_{12}A is 2.54(8) Å⁷ and that of $\text{Ag}_{2.9}\text{Zn}_{4.6}\text{A}$ is 2.29(4) Å⁸. The carbon atoms associated with Ag^+ ions should be different from those associated with Ca^{2+} ions but these two could not be resolved crystallographically. Therefore, carbon atom position at C(1) will be an average position. Ag(1)-C(1) distances must be determined shorter while Ca(1)-C(1) distances must be determined longer. Nevertheless, the metallic cation-carbon bond lengths indicate that each ethylene is firmly held by the Ag^+ ion and loosely bound to the Ca^{2+} ion.

The bonding between metallic cations and ethylene is usually described in terms of the Chatt-Dewar model.¹⁹ An initial σ bond is formed between the filled π orbital of ethylene and an empty σ -acceptor orbital of the metal (for example, 5s orbital of Ag^+ ion and 4s orbital of Ca^{2+}). Accumulated negative charge on the metal then is "back-donated" by $d\pi$ orbitals of the metal to a π -acceptor orbital of ethylene. The filled 4d orbital of Ag^+ ion (ionic radii = 1.26 Å)¹⁵ reaches sufficiently far out in space to overlap effectively with π^* orbital ethylene. However, almost empty 3d orbitals of Ca^{2+} ($r = 0.99$ Å)¹⁵ do not overlap with π^* orbital of ethylene as 4d orbitals of Ag^+ ion do with π^* orbital of ethylene. The Ag^+ -C distance, 2.21(1) Å is much shorter than the Ca^{2+} -C distance, 3.06(2) Å. Therefore Ca^{2+} - C_2H_4 complexes in zeolite A have much weaker interaction than Ag^+ - C_2H_4 complexes.

The present results are consistent with those of Carter *et al.*²⁰ They have studied the sorption of ethylene at room temperature onto a series of ion-exchanged synthetic near faujasites by infrared spectroscopy and microcalorimetry. They found that C_2H_4 molecules form laterally held π complexes of symmetry C_2 . Of the transition metal ions examined, Ag^+ and Cd^{2+} were found to hold C_2H_4 most strongly. Furthermore, the adsorbed ethylene molecules are reported

to be freely rotating in all case, except in its Ag^+ complex.

Because of the combined effects of disorder (the averaging of Al and Si positions into a single (Si, Al) position and of the oxide ion positions as though the coordination spheres of Si and Al were the same size) and moderately high thermal motions, the ethylenic double bond length 1.27(3) Å is a little bit shorter and inaccurately determined. However the esd of this bond length is high, so may be acceptable. This result is very similar to those found in the ethylene sorption complexes of $\text{Co}_4\text{Na}_4\text{-A}$, 1.21(11) Å and that $\text{Ag}_{12}\text{-A}$, 1.19(12) Å.³⁶ For comparison, the C=C bond length in ethylene gas is 1.334 Å.²¹

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References

1. R. E. Riley and Seff, *Inorg. Chem.*, **13**, 1355 (1974).
2. R. Y. Yanagida, T. B. Vance, and K. Seff, *Inorg. Chem.*, **13**, 721 (1974).
3. P. E. Riley, K.B. Kunz, and K. Seff, *J. Am. Chem. Soc.*, **97**, 537 (1975).
4. P. E. Riley and K. Seff, *J. Am. Chem. Soc.*, **95**, 8180 (1973).
5. P. E. Riley and K. Seff, *Inorg. Chem.*, **14**, 714 (1975).
6. Y. Kim and K. Seff, *J. Am. Chem. Soc.*, **100**, 175 (1978).
7. M. S. Jeong, J. Y. Park, U. S. Kim, and Y. Kim, *J. Korean Chem. Soc.*, **34**, 189 (1991).
8. S. B. Jang, S. D. Moon, J. Y. Park, U. S. Kim, and Y. Kim, *Bull. Korean Chem. Soc.*, **13**, 76 (1992).
9. J. F. Charnell, *J. Cryst. Growth*, **8**, 291 (1971).
10. K. Seff and M. D. Mellum, *J. Phys. Chem.*, **88**, 3560 (1984).
11. K. Seff, *Acc. Chem. Res.*, **9**, 121 (1976).
12. Calculations were performed using the "Structure Determination Package Program" written by B. A. Frentz, and Y. Enraf-Nonius, Netherlands, 1987.
13. "International Tables for X-ray Crystallography", Vol. II, Kynoth Press, Birmingham, England, p. 302, 1974.
14. Y. Kim, S. H. Song, and K. Seff, *J. Phys. Chem.*, **95**, 5959 (1990).
15. "Handbook of Chemistry and Physics", 70th ed., The Chemical Rubber Co., Cleveland, Ohio, 1989/1990, p. F-187.
16. P. A. Doyle and P. S. Turner, *Acta Crystallogr. Sect. A*, **24**, 390 (1974).
17. "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, pp. 73-87.
18. Reference 17, pp. 149-150.
19. (a) J. Chatt, *J. Chem. Soc.*, 3340 (1949); (b) J. Chatt and R. G. Wilkins, *Ibid.*, 2639 (1952); (c) J. Chatt and L. A. Duncanson, *Ibid.*, 2939 (1953); (d) M. J. S. Dewar, *Bull. Soc. Chem. Fr.*, **18**, C71 (1971).
20. J. L. Carter, J. C. Yates, P. J. Lucchesi, J. J. Elliott, and V. Kevorkian, *J. Phys. Chem.*, **70**, 1126 (1966).
21. L. E. Sutton, "Interatomic Distance and Configuration in Molecules and Ions", The Chemical Society, 1985, p. M-129.

A New Chiral Synthetic Route to (+)-Isocarbacyclin

Hokoon Park* and Yong Sup Lee

*Organic Chemistry Laboratory I, Korea Institute of Science & Technology,
P.O. Box 131 Cheongryang, Seoul 136-650*

Sang Chul Shim

*Department of Chemistry, Korea Advanced Institute of Science & Technology,
Taejeon 305-701. Received August 2, 1992*

A synthetic route to (+)-isocarbacyclin starting from (–)-tricyclo[3.3.0.0^{2,8}]octan-3-one **6** is described. The key intermediate **4** has been synthesized from **6** by a sequential introduction of methoxycarbonyl group at C-12 and the oxygen functionality at C-9 α (PG numbering) for the construction of α - and ω -side chain, and then converted to isocarbacyclin methyl ester **2**.

Introduction

Prostacyclin **3** is a potent inhibitor of platelet aggregation.¹ In human platelet-rich plasma, prostacyclin is 50 and 20 times more active than PGE_2 and PGD_2 , respectively. However, prostacyclin can not be used for therapeutic purposes as it is, since it is very unstable due to the presence of

an enol ether group.

Since the discovery of prostacyclin, considerable attention has been focused on the design of stable prostacyclin analogues which still retain the sufficient biological activity. Among them, isocarbacyclin [**1**, 9(O)-methano- $\Delta^{6,9(\alpha)}$ -PGI₁] has recently been introduced as a promising therapeutic agent for cardiovascular disease.² Afterwards, a number of