

## Reaction of Dehydrated $\text{Ag}_2\text{Ca}_5\text{-A}$ with Cesium. Crystal Structures of Fully Dehydrated $\text{Ag}_2\text{Ca}_5\text{-A}$ and $\text{Ag}_2\text{Cs}_{10}\text{-A}$

Yang Kim\*, Seong Hwan Song, Jong Yul Park, and Un Sik Kim

Department of Chemistry, Pusan National University, Pusan 609-735. Received January 9, 1989

Two crystal structures of dehydrated  $\text{Ag}^+$  and  $\text{Ca}^{2+}$  exchanged zeolite A,  $\text{Ag}_2\text{Ca}_5\text{-A}$ , reacting with 0.01 Torr of Cs vapor at 200 °C for 2 hours and 0.1 Torr of Cs vapor at 250 °C for 48 hours, respectively, have been determined by single crystal X-ray diffraction techniques. Their structures were solved and refined in the cubic space group  $Pm\bar{3}m$  at 21(1) °C. The stoichiometry of first crystal was  $\text{Ag}_2\text{Ca}_5\text{-A}$  ( $a = 12.294(1)\text{Å}$ ), indicating that Cs vapor did not react with cations in zeolite A and that of second crystal was  $\text{Ag}_2\text{Cs}_{10}\text{-A}$  ( $a = 12.166(1)\text{Å}$ ), indicating that all  $\text{Ca}^{2+}$  ions were reduced by Cs vapor and replaced by  $\text{Cs}^+$  ions. Full-matrix least-squares refinements of  $\text{Ag}_2\text{Ca}_5\text{-A}$  and  $\text{Ag}_2\text{Cs}_{10}\text{-A}$  has converged to the final error indices,  $R_1 = 0.041$  and  $R_2 = 0.048$  with 227 reflections, and  $R_1 = 0.117$  and  $R_2 = 0.120$  with 167 reflections, respectively, for which  $I > 3\sigma(I)$ . In the structure of  $\text{Ag}_2\text{Ca}_5\text{-A}$ , both  $\text{Ag}^+$  ions and  $\text{Ca}^{2+}$  ions lie on two crystal symmetrically independent threefold axis sites on the 6-rings; 2  $\text{Ag}^+$  ions are recessed 0.33 Å from the (111) planes of three O(3) oxygens and 5  $\text{Ca}^{2+}$  ions lie on the nearly center of each 6-oxygen planes. In the structure of  $\text{Ag}_2\text{Cs}_{10}\text{-A}$ ,  $\text{Cs}^+$  ions lie on the 5 different crystallographic sites. 3  $\text{Cs}^+$  ions lie at the centers of the 8-rings at sites of  $D_{4h}$  symmetry. 6  $\text{Cs}^+$  ions lie on the threefold axes of unit cell: 4  $\text{Cs}^+$  ions are found deep in the large cavity and 2  $\text{Cs}^+$  ions are found in the sodalite cavity. One  $\text{Cs}^+$  ion is found in the large cavity near a 4-ring.

### Introduction

In 1956, Breck *et al.* reported that  $\text{Cs}^+$  ion exchange into zeolite A with a 100% excess of  $\text{Cs}^+$  (0.14 M aqueous solution at 90 °C) resulted in the replacement of only 31% the  $\text{Na}^+$  ions in the zeolite A structure.<sup>1</sup> Barrer *et al.* increased the level of  $\text{Cs}^+$  exchange to 45% by exposing the zeolite to successive concentrated aqueous solution at 25 °C.<sup>2</sup> However, the levels of  $\text{Cs}^+$  exchange into zeolite A were gradually increased from 7/12 to 11/12 by various ion-exchange strategies during the last decade.<sup>3-5</sup> In 1987, Seff and Heo succeeded to prepare the fully dehydrated, fully  $\text{Cs}^+$ -exchanged zeolite A through the reduction of all  $\text{Na}^+$  ions in  $\text{Na}_{12}\text{-A}$  by cesium vapor. Complete reactions of  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Co}^{2+}$  ions in the dehydrated zeolite A with Cs vapor is readily achieved at 250 °C or higher.<sup>6,7</sup> However, when  $\text{Ag}^+$  ions in dehydrated  $\text{Ag}_{12}\text{-A}$  were exposed to ca 0.1 Torr of Cs vapor at 220 °C, the resulted crystal showed no single crystal diffraction pattern, indicating that the crystallinity of zeolite A structure was lost.<sup>8</sup>

$\text{Ag}^+$  ions in zeolite A can be reduced by heating, by reaction with reducing agents, or by sorption of metal atoms.<sup>9,10</sup> In the structure of dehydrated  $\text{Ag}_6\text{Na}_6\text{-A}$ , treated with 50 Torr of  $\text{H}_2$  at room temperature, 1.27 ( $\text{Ag}_3$ )<sup>+</sup> clusters and 0.7 ( $\text{Ag}_3$ )<sup>2+</sup> clusters per unit cell were found in the large cavity.<sup>9</sup> In the structure of  $\text{Ag}_{4.6}\text{Na}_{7.4}\text{-A}$ , vacuum dehydrated and treated with  $\text{H}_2$  at 350 °C, ( $\text{Ag}_6$ )<sup>3+</sup> clusters of low symmetry were found in the large cavity.<sup>10</sup>

Barrer and Whiteman reported that large quantities of mercury vapor could be sorbed by  $\text{Ag}^+$ -exchanged zeolite X without damaging the zeolite structure.<sup>11</sup> However the uptake of mercury vapor by  $\text{Ag}^+$ -exchanged zeolite A at 70° and 150 °C, respectively, resulted in the lose of crystallinity of zeolite A structure.<sup>12</sup>

This work was done with the hope that Cs vapor would reduce the  $\text{Ag}^+$  ions and  $\text{Ca}^{2+}$  ions in zeolite A and form Ag atoms and clusters which might be examined crystallographically. If  $\text{Ag}^+$  ions are not reduced but  $\text{Ca}^{2+}$  ions are only

reduced by Cs vapor, the relative preference of  $\text{Cs}^+$  ions and  $\text{Ag}^+$  ions for the coordination sites available within the zeolite will be learned. The resulted crystal structure of  $\text{Ag}_2\text{Cs}_{10}\text{-A}$  can be accurately determined for two reasons: (1)  $\text{Ag}^+$  and  $\text{Cs}^+$  are powerful scatters of X-ray, therefore it is easy to distinguish  $\text{Ag}^+$  from  $\text{Cs}^+$ . So the ions are relatively easy to locate, and (2) the ionic radii of  $\text{Ag}^+$  and  $\text{Cs}^+$  are quite different, *i.e.*  $\text{Ag}^+ = 1.26\text{Å}$  and  $\text{Cs}^+ = 1.67\text{Å}$ .<sup>13</sup>

### Experimental

Crystals of zeolite 4A were prepared by Charnell's method.<sup>14</sup> To prepare exchanged crystals of composition  $\text{Ag}_2\text{Ca}_5\text{-A}$ , an exchange solution of  $\text{AgNO}_3$  and  $\text{Ca}(\text{NO}_3)_2$  in the mole ratio of 1 to 1000, with a total concentration of 0.05 M, was used. This ratio is obtained by the previous study of the crystal structures of dehydrated  $\text{Ag}_2\text{Ca}_5\text{-A}$  and  $\text{Ag}_7\text{Ca}_{2.5}\text{-A}$  which were prepared using exchange solution in which  $\text{AgNO}_3/\text{Ca}(\text{NO}_3)_2$  was 1:1000 and 1:50, respectively.<sup>15</sup>

Ion exchange was accomplished allowing the solution to flow past each crystal at a velocity of approximately 0.5 cm/sec for 4 days.

After exchange, each crystal remained colorless. After crystal 1 and 2 were dehydrated at 360 °C and  $2 \times 10^{-6}$  Torr for 2 days, cesium vapor (99.98% purity; Johnson Matthey Inc.) was introduced by distillation from a side-arm break-seal ampule to the glass-tube extension of the crystal-containing capillary. This glass reaction vessel was then sealed off under vacuum and placed within two cylindrical coaxially attached horizontal arm. The oven about the crystal was always maintained at a higher temperature than that about the cesium metal so that cesium would not distilled into the crystal. The first reaction, carried out at 200 °C (ca 0.01 Torr of cesium vapor) (cesium source at 155 °C) for 2 hours, resulted in no reaction (crystal 1).<sup>16</sup> A second crystal of  $\text{Ag}_2\text{Ca}_5\text{-A}$  was prepared similarly and allowed to react at a higher temperature, 250 °C (ca 0.1 Torr of cesium vapor) (cesium source at 210 °C) for 48 hours (crystal 2). The resulted crystal was

**Table 1.** Positional, Thermal<sup>a</sup>, and Occupancy ParametersCrystal 1. Dehydrated Ag<sub>2</sub>Ca<sub>5</sub>-A treated with 0.1 Torr of Cs vapor at 210 °C for 48 hours (structure of Ag<sub>2</sub>Cs<sub>10</sub>-A)

Atom	Wyckoff Position	<i>x</i>	<i>y</i>	<i>z</i>	$b\beta_{11}$ or $\beta_{iso}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	Occupancy	
											varied	fixed
(Si,Al)	24( <i>k</i> )	0	1827(8)	3715(7)	41(6)	37(6)	33(6)	0	0	30(10)		24.0
O(1)	12( <i>h</i> )	0	2340(30)	5000	210(60)	90(40)	40(30)	0	0	0		12.0
O(2)	12( <i>i</i> )	0	2830(20)	2830(20)	130(40)	70(20)	70(20)	0	0	-100(60)		12.0
O(3)	24( <i>m</i> )	1080(10)	1080(10)	3400(20)	50(10)	50(10)	150(30)	-20(30)	10(30)	10(30)		24.0
Ag(1)	8( <i>g</i> )	1870(30)	1870(30)	1870(30)	250(20)	250(20)	250(20)	120(60)	120(60)	120(60)	1.62(12)	2.0
Cs(1)	3( <i>c</i> )	0	5000	5000	320(20)	76(5)	76(5)	0	0	0	3.20(10)	3.0
Cs(2)	8( <i>g</i> )	2837(5)	2837(5)	2837(5)	94(4)	94(4)	94(4)	-1(10)	-1(10)	-1(10)	4.11(8)	4.0
Cs(3)	8( <i>g</i> )	980(20)	980(20)	980(20)	310(20)	310(20)	310(20)	260(50)	260(50)	260(50)	2.05(7)	2.0
Cs(4)	24( <i>m</i> )	3520(40)	3520(40)	4510(50)	10						1.20(10)	1.0

Crystal 2. Dehydrated Ag<sub>2</sub>Ca<sub>5</sub>-A treated with 0.01 Torr of Cs vapor at 155 °C

Atom	Wyckoff Position	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	Occupancy	
											varied	fixed
(Si,Al)	24( <i>k</i> )	0	1831(2)	3712(2)	34(1)	21(1)	17(1)	0	0	9(3)		24.0
O(1)	12( <i>h</i> )	0	2156(7)	5000	61(7)	45(7)	43(7)	0	0	0		24.0
O(2)	12( <i>i</i> )	0	2852(6)	2852(6)	120(10)	42(4)	42(4)	0	0	40(10)		12.0
O(3)	24( <i>m</i> )	1114(3)	1114(3)	3369(5)	51(3)	51(3)	45(5)	30(9)	1(6)	1(6)		24.0
Ag(1)	8( <i>g</i> )	2020(3)	2020(3)	2020(3)	50(2)	50(2)	50(2)	40(4)	40(4)	40(4)	2.02(2)	2.0
Ca(1)	8( <i>g</i> )	1812(6)	1812(6)	1812(6)	172(3)	172(3)	172(3)	279(2)	279(2)	279(2)	5.20(7)	5.0

<sup>a</sup> Positional and isotropic thermal parameters are given  $\times 10^4$ . Numbers in parentheses are the esd's in units of the least significant digit given for the corresponding parameter. <sup>b</sup> The anisotropic temperature factor =  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$ . <sup>c</sup> Occupancy factors given as the number of atoms or ions per unit cell. Occupancy for (Si) = 12; occupancy for (Al) = 12.

sealed off from the reaction vessel by torch after cooling to room temperature.

The space group *Pm3m* (no systematic absences) was used throughout this work for reasons discussed previously.<sup>17,18</sup> Preliminary crystallographic experiments and subsequent data collection were performed with an Enraf-Nonius four-circle computer controlled CAD-4 diffractometer, equipped with a graphite monochromator, a pulse-height analyzer and a PDP micro 11/73 computer. Molybdenum radiation ( $K_{\alpha 1}$ ,  $\lambda = 0.70930$  Å;  $K_{\alpha 2}$ ,  $\lambda = 0.71359$  Å) was used for all experiments. The unit cell constant, as determined by a least-squares refinement of 25 intense reflections for which  $18^\circ < 2\theta < 25^\circ$  is 12.294(1) Å for Ag<sub>2</sub>Ca<sub>5</sub>-A and 12.166(1) Å for Ag<sub>2</sub>Cs<sub>10</sub>-A, respectively. Reflections from two intensity-equivalent regions of reciprocal space ( $hkl, h \leq k \leq l$ ; and  $hkl, h \leq l \leq k$ ) were examined using  $\omega$ - $2\theta$  scan technique. The data were collected using variable scan speeds. Most reflections were observed at the slow scan speeds, ranging between 0.150° and 0.260° in  $\omega$  min<sup>-1</sup>. The intensities of three reflections in diverse regions of reciprocal space were recorded after every three hours to monitor crystal and X-ray source stability. Only small, random fluctuation of these check reflections were noted during the course of data collection. For each region of reciprocal space, the intensities of all lattice points for which  $2\theta < 70^\circ$  for Ag<sub>2</sub>Ca<sub>5</sub>-A and  $2\theta < 60^\circ$  for Ag<sub>2</sub>Cs<sub>10</sub>-A, respectively, were recorded. The raw data from each region were corrected for Lorentz and polarization effects including that due to incident beam monochromatization; the reduced intensities were merged and the resultant estimated standard deviations were assigned to each average reflection by the

computer programs, PAINT and WEIGHT.<sup>19</sup> An absorption correction was not applied. Only the 922 pairs of reflections for the Ag<sub>2</sub>Ca<sub>5</sub>-A and 761 for the Ag<sub>2</sub>Cs<sub>10</sub>-A, only 227 and 167 pairs, for which  $I > 3\sigma(I)$ , respectively, were used in subsequent structure determination.

## Structure Determination

**(a) Dehydrated Ag<sub>2</sub>Ca<sub>5</sub>-A Reacting with 0.01 torr of Cs Vapor at 200°C for 2 hours.** Full-matrix least-squares refinement was initiated using the atomic parameters of the framework atoms ((Si,Al), O(1), O(2) and O(3)) of dehydrated and partially decomposed Ag<sub>12</sub>-A.<sup>20,21</sup> Anisotropic refinement of the framework atoms converged to an  $R_1$  index,  $(\sum |F_o - |F_c||) / \sum F_o$ , of 0.323 and a weighted  $R_2$  index,  $(\sum w(F_o - |F_c|)^2) / \sum w F_o^2$  of 0.42. A subsequent difference Fourier map revealed one large threefold axis peak at (0.202, 0.202, 0.202) of height 7.6(2) eÅ<sup>-3</sup>. Inclusion of this peak as Ag(1) lowered the error indices to  $R_1 = 0.127$  and  $R_2 = 0.173$  (see Table 1). A difference Fourier map revealed a peak at (0.181, 0.181, 0.181) of height 3.6(2) eÅ<sup>-3</sup>. Simultaneous positional, thermal and occupancy refinement including this position converged to  $R_1 = 0.041$  and  $R_2 = 0.047$ . The occupancies of these cations per unit cell refined to Ag(1) = 2.02(2) and Ca(1) = 5.20(7). These were fixed at Ag(1) = 2.0 and Ca(1) = 5.0. The final  $R$  values were  $R_1 = 0.041$  and  $R_2 = 0.048$ . The final difference map was featureless except one at origin (0.0, 0.0, 0.0) with peak height of 2.2(5) eÅ<sup>-3</sup>.

**(b) Ag<sub>2</sub>Ca<sub>5</sub>-A Reacting with 0.1 Torr of Cs Vapor at 250°C for 48 hours. Crystal Structure of Ag<sub>2</sub>Cs<sub>10</sub>-A.** Full

**Table 2.** Selected Interatomic Distances(Å) and Angles(deg) $^\circ$  of Dehydrated  $\text{Ag}_2\text{Ca}_5\text{A}$  treated with 0.01 Torr of Cs vapor at 200°C for 90 minutes and  $\text{Ag}_2\text{Cs}_{10}\text{A}$ 

	$\text{Ag}_2\text{Ca}_5\text{A}$	$\text{Ag}_2\text{Cs}_{10}\text{A}$
(Si,Al)-O(1)	1.633(4)	1.69(1)
(Si,Al)-O(2)	1.641(6)	1.63(3)
(Si,Al)-O(3)	1.683(4)	1.64(1)
Ag(1)-O(3)	2.288(5)	2.30(2)
Ca(1)-O(3)	2.267(6)	
Cs(1)-O(1)		3.24(3)
Cs(1)-O(2)		3.73(2)
Cs(2)-O(3)		3.09(1)
Cs(3)-O(3)		2.95(2)
Cs(4)-O(1)		4.55(5)
Cs(4)-O(3)		4.40(4)
O(1)-(Si,Al)-O(2)	116.0(4)	109(1)
O(1)-(Si,Al)-O(3)	111.8(3)	116(1)
O(2)-(Si,Al)-O(3)	103.9(2)	104.8(8)
O(3)-(Si,Al)-O(3)	109.0(2)	106.7(8)
(Si,Al)-O(1)-(Si,Al)	151.7(7)	136(3)
(Si,Al)-O(2)-(Si,Al)	170.2(4)	173(1)
(Si,Al)-O(3)-(Si,Al)	142.2(3)	146(1)
O(3)-Ag(1)-O(3)	118.0(1)	120.0(6)
O(3)-Ca(1)-O(3)	119.7(2)	
O(1)-Cs(1)-O(2)		45.1(3)
O(3)-Cs(2)-O(3)		80.1(5)
O(3)-Cs(3)-O(3)		84.9(4)
O(1)-Cs(4)-O(3)		36.5(5)

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

matrix least-squares refinement of the structure was commenced using the atomic parameters learned from the previous crystal of  $\text{Ag}_2\text{Ca}_5\text{A}$ . Anisotropic refinement of framework atoms converged to  $R_1 = 0.506$  and  $R_2 = 0.594$ . An examination of a difference Fourier map revealed three large peaks; two along threefold axes ( $x, x, x$ ) at  $x = 0.28$  (density =  $10.1(2) \text{ e}\text{\AA}^{-3}$  and  $x = 0.098$  (density =  $6.2(2) \text{ e}\text{\AA}^{-3}$ ) and third at the center of 8-oxygen ring at (0.0, 0.5, 0.5) with electron density of  $18.4(3) \text{ e}\text{\AA}^{-3}$ . Anisotropic refinement of the framework atoms and the Cs<sup>+</sup> ions at Cs(1), Cs(2), and Cs(3) converged to  $R_1$  and  $R_2$  indices of 0.143 and 0.205, respectively (see Table 1). A subsequent difference Fourier map revealed the position at Ag(1) with a peak height of  $2.9(2) \text{ e}\text{\AA}^{-3}$ . Inclusion of the peak at Ag(1) lowered the error indices to  $R_1 = 0.139$  and  $R_2 = 0.160$ . A difference Fourier map revealed a possible Cs<sup>+</sup> ion at (0.35, 0.35, 0.5). This peak was refined with unusually large thermal parameter of Cs(4),  $40(9) \text{ \AA}^2$ , suggested that the  $z$  coordinate of Cs(4) should be allowed to refine off the mirror plane 0.5. This was done, and in a refinement with all positional and thermal parameters free to vary, except that occupancy of all atoms and the isotropic thermal parameter of Cs(4) were fixed at the value given in Table 2. Cs(4) refined to (0.352, 0.352, 0.4510) with  $R_1 = 0.117$  and  $R_2 = 0.120$ . The final difference map was featureless except one at origin (0.0, 0.0, 0.0) with a peak height of  $2.2(5) \text{ e}\text{\AA}^{-3}$ .

For all structures, the full-matrix least-squares program

**Table 3.** Deviation of Atoms(Å) from the (111) Plane at O(3) of Dehydrated  $\text{Ag}_2\text{Ca}_5\text{A}$  treated with 0.01 Torr of Cs vapor at 200°C for 90 minutes and  $\text{Ag}_2\text{Cs}_{10}\text{A}$ 

	$\text{Ag}_2\text{Ca}_5\text{A}$	$\text{Ag}_2\text{Cs}_{10}\text{A}$
O(2)	0.076(4)	0.065(14)
Ag(1)	0.329(2)	0.036(18)
Ca(1)	-0.115(4)	
Cs(2)		2.069(4)
Cs(3)		-1.847(17)

A positive deviation indicates that the atom lies on the same side of the planes as the origin.

used minimized  $\Sigma w(F_o - |F_c|)^2$ , the weight  $w$  of an observation was the reciprocal square of  $\sigma(F_o)$  its standard deviation. Atomic scattering factors for Cs<sup>+</sup>, Ag<sup>+</sup>, Ca<sup>2+</sup>, O<sup>-</sup> and (Si,Al)<sup>1.75+</sup> were used.<sup>22</sup> The function describing (Si,Al)<sup>1.75+</sup> is the mean of the Si<sup>0</sup>, Si<sup>4+</sup>, Al<sup>0</sup>, and Al<sup>3+</sup> function. All scattering factors were modified to account for the anomalous dispersion<sup>23</sup>. The final structural parameters and selected interatomic distances and angles are presented in Table 1 and 2, respectively.

## Discussion

**(a) Dehydrated  $\text{Ag}_2\text{Ca}_5\text{A}$  Treated with Cs Vapor at 200°C for 90 Minutes.** In this structure, Ag<sup>+</sup> ions at Ag(1) and Ca<sup>2+</sup> ions at Ca(1) are on the threefold axes of unit cell and associated with 6-rings oxygens.<sup>24</sup> Ag(1) is 2.288(5) Å from three O(3)'s, less than the sum of the conventional ionic radii of Ag<sup>+</sup> and O<sup>2-</sup>, 2.58 Å.<sup>13</sup> Similarly, Ca(1) is 2.267 Å to three O(3)'s, almost close to the sum of the conventional ionic radii of Ca<sup>2+</sup> and O<sup>2-</sup>, 2.31 Å.<sup>13</sup> Considering the sum of Ag<sup>+</sup> and O<sup>2-</sup> radii, Ag(1)-O(3) bonds are quite short and therefore quite covalent.

The 2 Ag<sup>+</sup> ions at Ag(1) are recessed 0.329 Å into large cavity from the (111) plane at O(3) (see Table 3). The 5 Ca<sup>2+</sup> ions at Ca(1) are correspondingly recessed 0.115 Å into the sodalite cavity. Bond angles, O(3)-Ag(1)-O(3) = 118.0(1)° and O(3)-Ca(1)-O(3) = 119.7(2)° indicate that Ag<sup>+</sup> ions and Ca<sup>2+</sup> ions have approximately trigonal planar bonding to their adjacent three framework oxygens, O(3)'s of the 6-ring (Figure 1).

In this structure, cations are occupied only at 6-ring sites. Three 8-ring sites and twelve 4-ring sites are empty. Since ionic radius of Ag<sup>+</sup> ion and that Ca<sup>2+</sup> ion are relatively small compared to Cs<sup>+</sup>, K<sup>+</sup> and Tl<sup>+</sup> ions, which are rather occupied at 8-ring sites, only 6-ring sites are occupied by Ag<sup>+</sup> ions and Ca<sup>2+</sup> ions.

In this crystal,  $\text{Ag}_2\text{Ca}_5\text{A}$  crystal was treated with 0.01 torr Cs vapor at 200 °C for 2 hours. Since Ag<sup>+</sup> and Ca<sup>2+</sup> were not reduced by Cs vapor in this study, it appears that the stronger reaction conditions are needed for reducing Ag<sup>+</sup> and Ca<sup>2+</sup> ions by Cs vapor.

**(b) Dehydrated  $\text{Ag}_2\text{Ca}_5\text{A}$  Treated with Cs Vapor at 250°C for 2 Days.** In the structure of vacuum-dehydrated  $\text{Ag}_2\text{Ca}_5\text{A}$  reacted with 0.1 Torr of Cs vapor at 250 °C for 48 hours, all Ca<sup>2+</sup> ions were reduced and replaced by Cs<sup>+</sup> ions; solvent-free ion exchange reaction only proceeded selectively to Ca<sup>2+</sup> ions under the present experimental conditions (Figure 2).

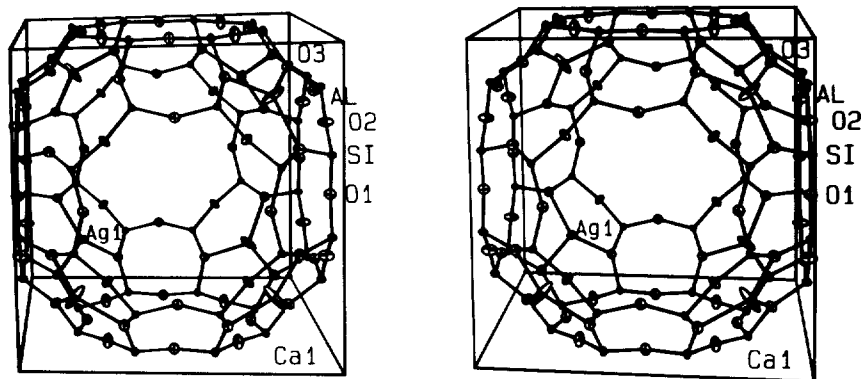


Figure 1. A stereoview of a large cavity of dehydrated  $\text{Ag}_2\text{Ca}_5\text{-A}$  treated with 0.01 Torr of Cs vapor. Ellipsoids of 20% probability.

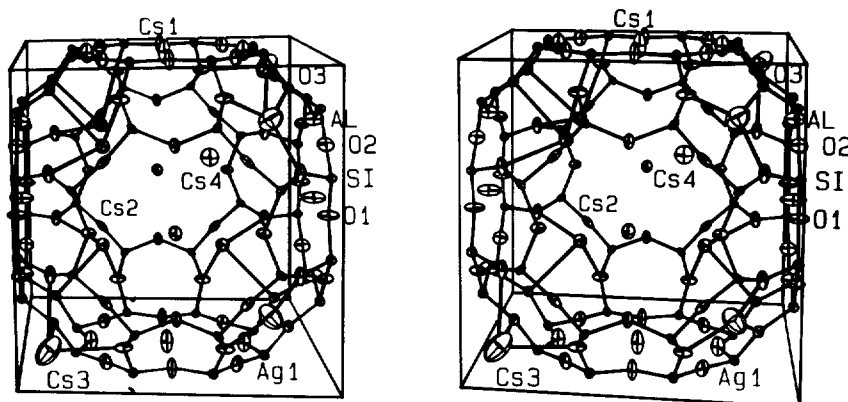


Figure 2. A stereoview of a large cavity of dehydrated  $\text{Ag}_2\text{Ca}_5\text{-A}$  treated with 0.1 Torr of Cs vapor. Ellipsoids of 20% probability are used.

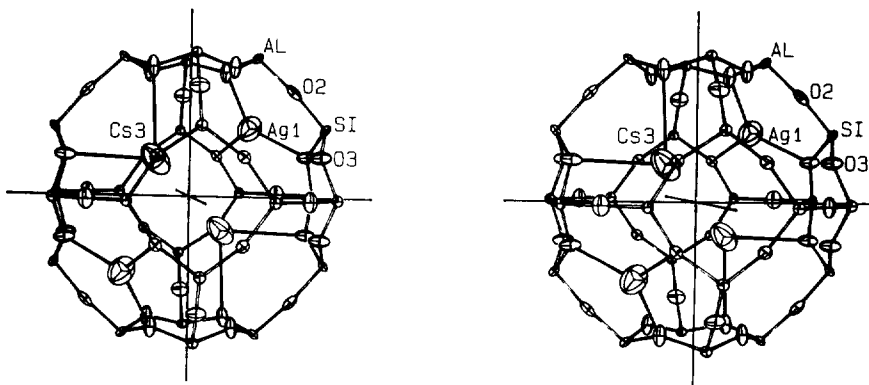


Figure 3. A stereoview of a sodalite unit of dehydrated  $\text{Ag}_2\text{Ca}_5\text{-A}$  treated with 0.1 Torr of Cs vapor. Ellipsoids of 20% probability are used.

Three  $\text{Cs}^+$  ions at Cs(1) fill the equipoints of symmetry  $C_{4h}$  ( $D_{4h}$  in  $Pm3m$ ) at the centers of the 8-rings, as they have in all previously reported  $\text{Cs}^+$ -exchanged zeolite A structure.<sup>6,7,25</sup> Each Cs(1) cation is  $3.24(3)\text{Å}$  from four O(1)'s oxygens and  $3.73(2)\text{Å}$  from four O(2)'s (see interatomic distances in Table 2). These distances are substantially longer than the sum of the ionic radii of  $\text{O}^{2-}$  and  $\text{Cs}^+$   $2.99\text{Å}$ . Theoretical calculations also support this observation of a potential energy minimum at these positions.<sup>26,27</sup>

Four  $\text{Cs}^+$  ions at Cs(2) are on threefold axes in the large cavity. Each  $\text{Cs}^+$  ion extends  $2.069\text{Å}$  into the large cavity from the (111) plane at O(3) and coordinates to three O(3) oxygens of the 6-ring at  $3.09(1)\text{Å}$  (Figure 2). Two  $\text{Cs}^+$  ions at Cs(3) are also on threefold axes and associated with 6-rings. The ion at Cs(3) is recessed  $1.847(17)\text{Å}$  into the sodalite cavi-

ty from the (111) plane at O(3). Each of these ions is associated with three O(3) oxygens at  $2.95(2)\text{Å}$  (Figure 3).

Two  $\text{Ag}^+$  ions at Ag(1) are on threefold axes and lie close to the 6-ring planes at O(3). This position is familiar, having been found in previous work. Ag(1) is  $2.30(2)\text{Å}$  from three O(3)'s.<sup>20,21</sup>

The twelfth cation at Cs(4) is statistically distributed over a 24-fold equipoint. This position is in the large cavity. This  $\text{Cs}^+$  ion is rather far from framework oxygens  $4.40(4)\text{Å}$  from O(3) probably because of repulsive interaction with the  $\text{Ag}^+$  ion in an adjacent 6-ring (also, less importantly, this distance may be virtual, a bit too long: this particular 4-ring may have a distorted geometry due to the presence of its  $\text{Cs}^+$  cation). Similar  $\text{Cs}^+$  ion was also observed in other zeolite structure.<sup>6,7</sup>

Recently the crystal structure of partially  $\text{Ag}^+$ -exchanged zeolite A,  $\text{Ag}_{3.2}\text{Na}_{8.8}\text{-A}$ , vacuum dehydrated at  $360^\circ\text{C}$  and then exposed to 0.1 torr of cesium vapor for 12 hours at  $250^\circ\text{C}$  has been studied.<sup>28</sup> In this crystal only  $\text{Na}^+$  ions were also reduced by Cs vapor and replaced by  $\text{Cs}^+$  ions. It appears that  $\text{Ag}^+$  ions are more stable than  $\text{Na}^+$  ions and  $\text{Ca}^{2+}$  ion in Cs vapor at  $250^\circ\text{C}$ . But when fully dehydrated, fully  $\text{Ag}^+$  exchanged zeolite A were exposed to 0.1 torr Cs vapor at  $250^\circ\text{C}$ , the resulting crystal showed no single crystal diffraction pattern, indicating that  $\text{Ag}^+$  ions are reduced by Cs vapor and migrated out of zeolite frameworks.<sup>8</sup> This exchange reaction using metal vapor may be viewed as a way of achieving ion exchange without the use of a solvent. This method of ion exchange allows problems of hydrolysis and overexchange to be circumvented. These problems are often encountered when ion exchange from aqueous solution is attempted.

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## The Molecular Structure and Conformational Stability of Cyclobutylmethyl Ketone by MM2

Mu Sang Lee\* and Young Mee Jung

Department of Chemistry, Teachers College, Kyungpook National University, Taegu 702-701

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The molecular structure of cyclobutylmethyl ketone ( $c\text{-C}_4\text{H}_7\text{COCH}_3$ ) has been investigated by molecular mechanics II (MM2). For the monosubstituted cyclobutane there are two possible ring conformations, the equatorial and axial form, but for the cyclobutylmethyl ketone the equatorial form is predominant conformation. For the  $\text{COCH}_3$  moiety there are two stable orientations which are the equatorial-gauche and the equatorial-trans form. The equatorial-gauche form where the  $\text{C}=\text{O}$  bond is nearly eclipsing (torsional angle  $\angle\text{C4-C3-C2-O10} = 14.5^\circ$ ) one of the  $\alpha\text{-C-C}$  bonds of the four-membered ring was preferred conformer with steric energy of 13.37 kcal/mol. The equatorial-trans form where the  $\text{C}=\text{O}$  bond is nearly eclipsing ( $\angle\text{C4-C3-C2-O10} = 145.0^\circ$ ) the  $\alpha\text{-C-H}$  bond of the four-membered ring was less stable conformer with steric energy of 15.40 kcal/mol.

### Introduction

Previous works by several groups have shown that halo-

cyclobutanes similar with cyclobutylmethyl ketone exist only as an equatorial conformer.<sup>1-7</sup>

For cyclobutylmethyl ketone two conformers, equato-