# Two Crystal Structures of Dehydrated Ag<sup>•</sup> and K<sup>•</sup> Exchanged Zeolite A, Ag<sub>12x</sub>K<sub>x</sub>-A, x = 1.3 and 2.7

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Two crystal structures of fully dehydrated silver and potassium exchanged zeolite A, stoichiometries of  $Ag_{9,3}K_{2,7}A$ (*a* = 12.282(2) Å) and  $Ag_{10,7}K_{1,3}$ Å (*a* = 12.287(2) A) per unit cell, have been determined from 3-dimensional x-ray diffraction data gathered by counter methods. All structures were solved and refined in the cubic space group *Pm3m* at 21(1) °C. The crystals of  $Ag_{9,3}K_{2,7}A$  and  $Ag_{10,7}K_{1,3}A$  were prepared by flow method using exchange solutions in which mole ratios of  $Ag_{9,3}K_{2,7}A$  and  $Ag_{10,7}K_{1,3}A$  were refined to yield the final error indices  $R_1 = 0.037$  and  $R_2 = 0.040$  with 321 reflections, and  $R_1 = 0.042$  and  $R_2 = 0.043$  with 371 reflections, repectively, for which  $I>3\sigma(I)$ . In both structures, eight  $Ag^+$  ions are found nearly at 6-ring centers and each  $Ag^+$  ion is nearly in the (1 1 1) plane at its O(3) ligands. The 8-ring sites are preferentially occupied by K<sup>+</sup> ions in both structures. 1.3 and 1.7 reduced silver atoms per unit cell were found inside of sodalite units of  $Ag_{9,3}K_{2,7}A$  and that of  $Ag_{10,7}K_{1,3}A$ , respectively. These reduced silver species were presumably formed from the reduction of  $Ag^+$  ions by oxide ions of residual water molecule or of the zeolite framework. These two crystals may be presented as hexasilver cluster in 21.7% and 28.3% of sodalite unit cells for  $Ag_{9,3}K_{2,7}A$  and  $Ag_{10,7}K_{1,3}A$ , repectively.

#### Introduction

Dehydrated zeolite A has a large empty space at the center of its unit cube, which is nearly spherical with a diameter of 11.4 Å and is called  $\alpha$ -cage.<sup>1,2</sup> This cage is surrounded by six eight-membered rings which lie on the corner of the cube and constitutes of window to the cage. The 8-ring cations in zeolite A may block three dimentional channel system. In commerical molecular sieve 3A and 4A, the 8-ring windows are blocked by K<sup>+</sup> and Na<sup>+</sup> ions, respectively.<sup>1</sup> Zeolite as ion exchanger have been extensively investigated in recent years.<sup>2</sup> Exchangeable cations in a zeolite framework have a unique and exciting environment. These cations must find suitable coordination sites, by using the relatively rigid aluminosilicate without reorganization as a polydendate ligand<sup>3</sup>.

Ag<sup>+</sup> ions in zeolite A are autoreduced upon dehydration to form uncharge silver clusters, the molecules Ag<sub>6</sub> each within a cube of eight Ag<sup>+</sup> ions, each near the plane of a sixoxygen ring<sup>4,5</sup> Hermerschmidt and Haul also identified these cluster in the sodalite cavity of dehydrated Ag<sup>+</sup>-exchanged zeolite A using epr spectroscopy<sup>6</sup> and their results were duplicated by Grobet and Schoonheydt<sup>7</sup>. This was reverified by the careful work of Morton and Preston who did esr measurements on isotropically pure samples of Ag<sub>12</sub>-A.<sup>8</sup>

Up to this time, no structural studies of mixed cation system of Ag<sup>+</sup> and K<sup>+</sup> ion exchanged zolite A have been reported. A detail knowledge of the structural fasts of Ag<sup>+</sup> and K<sup>+</sup> exchanged zeolite A could be most interesting because this can provide informations on the pore size of 8-ring and sorption properties of guest molecules. The present work is preliminary to later studies of the crystal structures of Ag<sub>12x</sub>K<sub>x</sub>·A (0<x<12) treated with H<sub>2</sub> or other guest molecules.

#### Experimental

Crystals of zeolite 4A were prepared by Charnell's method.<sup>9</sup> Each of two single crystals (0.08 mm on an edge)

was lodged in a fine glass capillary.

Crystals of  $Ag_{9,3}K_{2,7}A$  and  $Ag_{10,7}K_{1,3}A^{10}$  were prepared using exchange solutions in which mole ratios of AgNO<sub>3</sub> and KNO<sub>3</sub> were 1:5 and 1:10, respectively, with a total concentration of 0.05 M.

Ion exchange was accomplished allowing the solution to flow past each crystal at a velocity of approximately 1.0 cm/sec for 3 days at 23(1) °C. All the crystals were evacuated at 370 °C and  $P = 2 \times 10^{-6}$  Torr for 2 days. After cooling to room temperature, the crystal, still under vacuum was sealed in its capillary by a torch. Microscopic examination showed that both crystals became dull red.

Diffraction intensities were subsequently collected at 24 °C. The space group *Pm3m* (no systematic absences) was used throughout this work for reasons discussed previously.<sup>11</sup> An Enraf-Nonius 4-circle computer controlled CAD-4 diffractometer, equipped with scintillation counter, pulse-height analyzer, a PDP micro 11/73 computer, and a graphite monochromater was used. Molybdenum radiation ( $K_{\sigma1}$ ,  $\lambda = 0.70930$  Å;  $K_{\sigma2}$ ,  $\lambda = 0.71359$  Å) was used for all experiments. The unit cell constants, as determined by a least squares refinement of 2 $\theta$  intense reflections for which 20°<2 $\theta$ <32°, are 12.287(2) Å for Ag<sub>10.7</sub>K<sub>1.3</sub>·A and 12.282 (2) Å for Ag<sub>9.3</sub>K<sub>2.7</sub>A, respectively.

For each crystal, reflections from two intensity-equivalent regions of reciprocal space (hkl,  $h \le k \le l$  and lhk,  $l \le h \le k$ ) were examined using the  $\omega$ -2 $\theta$  scan technique. The data were collected using variable scan speeds. The maximum final scan speed was 5 minutes per one reflection. The intensities of three reflections in diverse regions of reciprocal space were recorded after every 100 reflections to monitor crystal and instrument stability. 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 deviation were assigned to each average reflection by the computer programs, PAINT and WEIGHT.<sup>12</sup> Of the 877 pairs of reflections for the dehydrated Ag<sub>10.7</sub>K<sub>1.3</sub><sup>-A</sup> and 373 for the dehydrated Ag<sub>9.5</sub>K<sub>2.7</sub>A, only 374 and 321 pairs,

Table 1.	"Positional,	Thermal, a	d Oc	cupancy l	Parameters of	f dehyı	drated A	810.7K1.3-A	
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Atom	Wyc. Posi.	x	у	z	<sup>\$</sup> β11	<b>\$ 22</b>	β33	\$ 12	<b>\$</b> 13	₿ <sub>23</sub>	Occupancy varied fixed
(Si, Al)	24( <b>k</b> )	0	1836(2)	3698(2)	24(1)	17(1)	15(1)	0	0	7(2)	24.
O(1)	12( <b>h</b> )	0	2150(9)	0.5	74(8)	72(8)	12(4)	0	0	0	12.0
O(2)	12(i)	0	2957(5)	2957(5)	38(5)	29(3)	29(3)	0	0	20(9)	12.0
O(3)	24( <b>m</b> )	1104(4)	1104(4)	3369(5)	44(3)	44(3)	42(4)	39(7)	32(5)	32(5)	24.0
Ag(1)	8(g)	1904(1)	1904(1)	1904(1)	78(1)	78(1)	78(1)	109(1)	109(1)	109(1)	7.91(3) 8.0
Ag(2)	6(e)	0	0	1700(3)	22(1)	22(1)	17(2)	0	0	0	1.77(2) 1.7
Ag(3)	12(1)	0	4330(20)	4330(20)	600(100)	280(30)	280(30)	0	0	150(90)	1.11(6) 1.0
K(1)	12(1)	0	4450(30)	4450(30)	40(20)	140(30)	140(30)	0	0	170(50)	1.31(8) 1.3

Table 2. "Positional, Thermal, and Occupancy Parameters of dehydrated Age,3 K2,7-A

Atom	Wyc. Posi.	X	y	2	* <i>β</i> 11	\$22	\$ <sub>33</sub>	<b>\$</b> 12	\$13	<b>\$2</b> 3	Occupa varied fi	
(Si, Al)	24( <b>k</b> )	0	1837(2)	3701(2)	23(1)	19(1)	17(1)	0	0	5(2)		24.0
<b>O(1)</b>	12( <b>h</b> )	0	2151(8)	0.5	61(7)	62(8)	20(5)	0	0	0		12.0
O(2)	12( <b>h</b> )	0	2963(5)	2963(5)	35(5)	32(3)	32(3)	0	0	27(9)		12.0
O(3)	24(m)	1116(3)	1116(3)	3370(5)	40(2)	40(2)	44(4)	27(7)	2 <b>6(</b> 5)	26(5)	2	24.0
Ag(1)	8(g)	1894(1)	1894(1)	1894(1)	71(1)	71(1)	71(1)	94(1)	94(1)	94(1)	7.81(5)	8.0
Ag(2)	6(e)	0	0	1702(34)	26(2)	26(2)	22(3)	0	0	0	1.36(2)	1.3
K(1)	12(1)	0	4510(10)	4510(10)	130(20)	180(20)	180(20)	0	0	- 10(40)	2.98(10)	

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

Table 3.	Selected Interatomic D	istances (Å	) and Angles (	dea)
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	$Ag_{10.7}K_{1.3}A$	Ag <sub>9.3</sub> K <sub>2.7</sub> A
(Si, Al)-O(1)	1.646(3)	1.641(3)
(Si, Al)-O(2)	1.651(4)	1.654(4)
(Si, Al)-O(3)	1.677(3)	1.681(3)
Ag(1)-O(3)	2.275(5)	2.262(5)
Ag(2)-O(3)	2.809(6)	2.821(6)
Ag(3)-O(1)	2.80(1)	
Ag(3)-O(2)	2.38(3)	
K(1)-O(1)	2.92(1)	2.97(2)
K(2)-O(2)	2.60(3)	2.69(1)
Ag(2)-Ag(2)	2.945(5)	2.957(5)
Ag(1)-Ag(2)	3.317(1)	3.299(1)
O(1)-(Si, Al)-O(2)	110.0(4)	109.6(4)
O(1)-(Si, Al)-O(3)	111.1(3)	111.0(3)
O(2)-(Si, Al)-O(3)	108.3(2)	107.9(2)
O(3)-(Si, Al)-O)3)	108.0(3)	109.2(3)
(Si, Al)-O(1)-(Si, Al)	152, 9(7)	152.7(7)
(Si, Al)-O(2)-(Si, Al)	156.9(4)	156.4(4)
(Si, Al)-O(3)-(Si, Al)	144.1(3)	143.2(3)
O(3)-Ag(1)-O(3)	119.8(1)	119.9(2)
O(3)-Ag(2)-O(3)	57.8(1)	58.2(1)
Ag(1)-Ag(2)-Ag(1)	89.67(2)	89.71(2)

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

for which  $I > 3\sigma(I)$ , respectively, were used in subsequent structure determinations.

The initial structural parameters used in least-squares refinement were those previously found for Ag<sup>+</sup>, Si, Al, and O atom in the structure of the dehydrated Ag<sub>12</sub>·A.<sup>5</sup> From the initial difference Fourier synthesis, Ag(2) and K(1) were located and refined (see Table 1 and 2). In zeolite A structure, 12 monopositive cations should be found per unit cell. 8 Ag<sup>+</sup> ions at Ag(1) are refined on the threefold axis of unit cell which is the maximum occupancy number at that position.

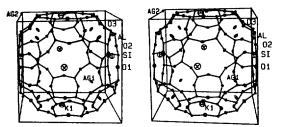
In the structure of  $Ag_{9,3}K_{2,7}A$ , 1.3 Ag species at Ag(2) and 2.7 K<sup>+</sup> ions at K(1) were refined with the constrainst that the sum of occupancies be 4.0. By similar techniques, 1.7 Ag species at Ag(2) and 1.0 Ag<sup>+</sup> ion at Ag(3) and 1.3K<sup>+</sup> ions at K(1) were located in the structure of Ag<sub>10,7</sub>K<sub>1,3</sub>A.

The structure of the dehydrated Ag<sub>9.3</sub>K<sub>2.7</sub>A and that of the dehydrated Ag<sub>10.7</sub>K<sub>1.3</sub>A was refined to give the final error indices  $R_1 = 0.037$  and  $R_2 = 0.040$ , and  $R_1 = 0.042$  and  $R_2 = 0.043$ , respectively.

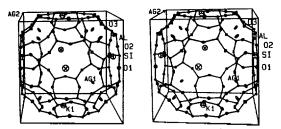
Atomic scattering factors for Ag<sup>+</sup>, Ag<sup>o</sup>, O<sup>-</sup>, K<sup>+</sup>, and (Si, Al)<sup>1.75+</sup> were used.<sup>13,14</sup> The function describing (Si, Al)<sup>1.75+</sup> is the mean of the Si<sup>o</sup>, Si<sup>4+</sup>, Al<sup>o</sup> and Al<sup>3+</sup> function. All scattering factors were modified to account for the real component ( $\Delta f$ ) of the anomalous dispersion correction.<sup>15,16</sup> Final position, thermal and occupancy parameters are presented in Table 1 and 2; bond angles and lengths are given in Table 3.

### Discussion

In the dehydrated  $Ag_{12x}K_x$ -A (where x = 2.7 and 1.3), eight Ag<sup>+</sup> ions at Ag(1) lie on threefold axes of the unit cell, each nearly at the center of one of the eight 6-rings per unit cell (see Figure 1 and 2 and Table 4). Each of these ions ap-



**Figure 1.** A stereoview of the large cavity of dehydrated  $Ag_{10.7}K_{1.3}A$  is shown with ellipsoids of 20% probability.



**Figure 2.** A stereoview of the large cavity of the dehydrated  $Ag_{9,3}K_{2,T}A$  is shown. All 6-ring sites are filled with 8 Ag<sup>+</sup> ions at Ag(1) and all 8-ring site and filled with K<sup>+</sup> ions. 70% of unit cells may have this arrangements and remaining 30% would have only 2 K<sup>+</sup> ions at K(1) per unit cell.

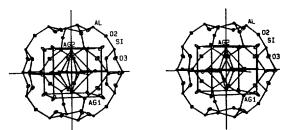
Table 4. Deviations of atoms (Å) from the (111) plane at O(3)

	Ag <sub>10.7</sub> K <sub>1.3</sub> A	Ag <sub>9.3</sub> K <sub>2.7</sub> A
O(2)	0.239(3)	0.231(3)
Ag(1)	0.095(1)	0.058(1)
Ag(2)	- 2.751(2)	- 2.765(3)

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

proachs three zeolite framework oxygens at O(3) at a distance of 2.275(5) Å for  $Ag_{10.7}K_{1.3}$ -A and that of 2.262(5) Å for  $Ag_{9.3}K_{2.7}$ -A, respectively. For comparison, the sum of the Ag<sup>+</sup> and O<sup>2-</sup> radii is 2.58Å.<sup>17</sup> It appears that the relatively short 2.27 Å bonds between the Ag<sup>+</sup> ions at Ag(1) and oxide ions of the zeolite framework, are quite covalent. On the surface of each sodalite unit, and consistent with its high symmetry,  $O_h$ , these eight Ag<sup>+</sup> ions lie at the corners of a cube, 4.68 Å on an edge.

On Ag<sup>+</sup> ion at Ag(3) for dehydrated Ag<sub>10.7</sub>K<sub>1.3</sub>-A is associated with 8-ring oxygens. This position is located in the plane of the 8-rings, but not at their center so that favorable approaches to framework oxygens may be made. This Ag\* ion is 2.38 (3) Å from the nearest framework oxygen at O(2) and 2.80(3) A from two oxygens at O(1). This coordination environment is relatively unsatisfactory, partly because its ligand atoms are all to one side, not arranged around it. Its large anisotropic thermal parameters also indicate it (see Table 2). 1.3 K\* ion at K(1) for Ag<sub>10.7</sub>K<sub>1.3</sub>-A and 2.7 K\* ions at K(1) for  $Ag_{9,3}K_{2,7}A$  lie close to the center of 8-ring plane compared with Ag<sup>+</sup> ion at Ag(3) for  $Ag_{10,7}K_{1,3}A$ . The K<sup>+</sup> ions of  $Ag_{10.7}K_{1.3}A$  and  $Ag_{9.3}K_{2.7}A$  are 2.60(3) Å and 2.69 (1) Å, apart from two adjacent O(2) and 2.92 (1) Å and 2.97(2)Å, from the nearest O(2), respectively (see Table III). If the K(1) were located at the center of the 8-rings, the K\*-O atomic distances of Ag<sub>10.7</sub>K<sub>1.3</sub> A and Ag<sub>9.3</sub>K<sub>2.7</sub> A would be 3.47Å and 3.50Å, to all four O(1)'s, respectively, and 3.56Å



**Figure 3.**  $(Ag^+)_8(Ag_6)$ . The octahedral hexasilver molecule at Ag(2) is stabilized by coordination to eight  $Ag^+$  ions at Ag(1). Ellipsoids of 20% probability are used. (The occupancy at Ag(2) is given as 1.7 in Table 1, together with the corresponding thermal parameters.)

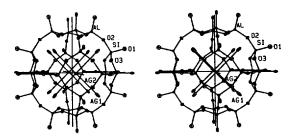


Figure 4. A stereoviews of sodalite unit containing two Ag<sup>4+</sup> clusters (heavy line) is shwon as an another possible alternative. Ellipsoids of 20% probability are used.

and 3.54Å, to all O(2)'s, respectively, as both distances are greater than the sum of the atomic radii of  $K^+$  and  $O^-$ , 2.65Å. Accordingly, it is reasonable that the K(1)'s are not found at the centers of the 8-rings.

The Ag(2) position is quite similar to that of the neutral silver atom in the structure of dehydrated partially decomposed Ag<sub>12</sub>·A.<sup>4,5</sup> The distances between Ag(2) and the nearest oxygens at O(3) are quite long, 2.806(6) Å for Ag<sub>10.7</sub>K<sub>1.3</sub>·A and 2.821 (6) A for Åg<sub>9.3</sub> K<sub>2.7</sub>·A, respectively, as it is compared to the corresponding ion to ion distances observed, and is about the same as was seen before between a neutral silver atom and framework oxide ions, O(3) as it is observed before.<sup>4,5</sup> The shortest available Ag(2)·Ag(2) distance, 2.95(1) Å, may be considered slightly longer than the Ag(2)·Ag(2) bond in natural silver metal, 2.889 Å<sup>18</sup> (see Figure 3).

The distance between Ag(1) and Ag(2) is ca 3.30 Å (see Table 3). This distance is equal to that of Ag<sup>+</sup>-Ag<sup>°</sup> in the structure of dehydrated Ag<sub>12</sub><sup>-</sup>A and similar to that of Ag<sup>+</sup>-Ag<sup>°</sup> in the structure of the dehydrated Ag<sub>6.5</sub>Tl<sub>5.5</sub>A.<sup>19</sup> This distance between Ag(1) and Ag(2) is too long to be an Ag<sup>°</sup>-Ag<sup>°</sup> bond and too short to be an unmoderated Ag<sup>+</sup>-Ag<sup>+</sup> contact. This is consistent with the conclusion (*vide supra*) that Ag(1) contains silver ions and Ag(3) silver stoms.

The Ag<sup>+</sup> ions which have been reduced are located at the least favorable positions such as an Ag<sup>+</sup> ions on opposite 4-ring site and Ag<sup>+</sup> ions on 8-ring sites. Neutral silver atom were also seen in the structures such as dehydrated  $Tl_xAg_{12x}$ -A (6<x<2),<sup>19,20</sup> Ag<sub>7.6</sub>Na<sub>4.4</sub>-A<sup>21</sup> and Ag<sub>12</sub>-A treated first with H<sub>2</sub> and then with O<sub>2</sub>, both at 330 °C.<sup>22</sup>

Since 1.3 silver atoms for  $Ag_{9,3}K_{2,7}A$  and 1.7 silver atoms for  $Ag_{10,7}K_{1,3}A$  are located inside of sodalite unit, this indicates that a neutral hexasilver cluster seems to be formed in about 22 and 28 percent of sodalite units, respectively. As an other alternative, Ag species at Ag(2) might interact with four of the eight Ag species at Ag(1) and form  $(Ag_5)^{4+}$  clusters. This  $(Ag_5)^{4+}$  cluster has  $C_{4\nu}$ , neark  $D_{4k}$  symmetry. The 1.3 or 1.7 Ag species at Ag(2) indicates that 30% of the sodalite units for  $Ag_{9,3}K_{2,7}A$  and 70% of sodalite units for  $Ag_{10,7}K_{1,3}$ -A have two  $(Ag_5)^{4+}$  clusters and the remaining 70% or 30% of the sodalite unit, respectively, may have only one  $(Ag_5)^{4+}$  clusters (see Figure 4).

A comparison of crystal structure of dehydrated  $Ag_{9,3}K_{2.7}A$  and that of  $Ag_{10.7}K_{1.3}A$ , indicates that K<sup>+</sup> ions preferentially occupy 8-ring site and  $Ag^+$  ions occupy 6-ring sites. This result is reasonable considering ionic radii of K<sup>+</sup> ion (1.33 Å) and that of  $Ag^+$  ion (1.26 Å). Larger K<sup>+</sup> ion will better fit to larger 8-ring site over small 6-ring site. These results are also consistent with the structures of  $Ag_9Cs_3A^{23}$  and  $Ag_9Rb_3A$ .<sup>24</sup> In both structures, larger three Cs<sup>+</sup> ions and three Rb<sup>+</sup> ions are located on the center of each 8-rings of unit cell.

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# Separation of Optical Isomers of Amino Acids with Addition of Benzyl-Lproline Copper (II) Chelate by Reversed Phase Liquid Chromatography

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Separation of optical isomers of dansyl amino acids by a reversed phase liquid chromatography has been accomplished by adding a copper (II) chelate of N-benzyl-L-proline to the mobile phase. The pH, the eluent composition and the concentration of copper (II) chelate all affect the optical separations. The elution orders between D and L DNS-amino acids were consistant except dansyl phenylalanine showing that D forms of DNS-amino acids elute earlier than L forms. These behaviors are different from the results obtained by the use of copper (II) proline. The retention mechanism for the optical separation of the dansyl amino acids can be explained by the equilibrium of liqand exchange and by hydrophobic interaction.

### Introduction

The resolution of optical isomers of amino acids by a high performance liquid chromatography (HPLC) has been interested, especially for the synthesis of peptides and the determination of the chemical structure. There are two different methods for the optical resolution of amino acids. The one is to use a chiral stationary phase (CSP) so that the chiral separation can be carried out by difference in the interaction in the solutes with the stationary phase between the optical