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탈수한 $Ag_{12-x}Na_x$-A(x=4, 6, 및 8)를 루비듐 증기로 처리한 세 가지 결정구조

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Three Crystal Structures of Dehydrated $Ag_{12-x}Na_x$-A(x=4, 6, and 8) Treated with Rubidium Vapor

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요 약. Ag^+ 이온이 부분적으로 이온 교환된 Zeolite A를 완전히 탈수한 결정 Ag_4Na_8-A, Ag_6Na_6-A 및 Ag_8Na_4-A를 250℃에서 4시간 동안 약 0.1 torr의 Rb 증기로 처리하였다. 세 가지의 결정구조는 22(1)℃에서 입방공간군 $Pm\bar{3}m$(단위세포상수 a가 각각 12.264(4) Å, 12.269(1) Å 및 12.332(3) Å임)을 이용하여 단결정 X-선회절법으로 해석하였고, Full-matrix 최소 자승법 정밀화 계산에서 각각 $I>3\sigma(I)$인 131개, 108개 및 94개의 독립반사를 사용하여 각각 최종오차인수 R=0.056, 0.068 및 0.070까지 정밀화시켰다. 각각의 구조에서 Rb^+ 이온은 3개의 다른 결정학적 위치에서 발견되었다. 단위세포당 3개의 Rb^+ 이온은 8-링 중심에 위치하고 있고, 약 6.0~6.8개의 Rb^+ 이온은 큰 동공의 6-링과 마주보는 위치의 3회 회전축상에서 발견되었으며 약 2.5개의 Rb^+ 이온은 소다라이트 동공내에서 발견되었다. 또한 Ag종은 2개의 서로 다른 결정학적 위치에서 발견되었다. 약 0.6~1.0개의 Ag^+ 이온은 4-링과 마주보는 위치에 존재하였고, 약 1.8~4.2개의 Ag 원자는 큰 동공의 중심 근처에 존재하였다. 이들 구조에서, 단위세포당 Ag 원자는 각각 1.8, 3.0 및 4.2개이고 이들은 큰 동공의 중심에서 헥사실버 클러스터를 형성하고 있다. 8-링 위치가 Rb^+ 이온으로 모두 차있어서 Ag^0가 골조 밖으로 이동하는 것을 막을 수 있다. 각각의 헥사실버 클러스터는 6-링과 8-링의 Rb^+ 이온 및 4-링의 Ag^+ 이온에 의해 안정화된다.

ABSTRACT. Three fully dehydrated partially Ag^+-exchanged zeolite A(Ag_4Na_8-A, Ag_6Na_6-A, and Ag_8Na_4-A) were treated at 250℃ with 0.1 torr Rb vapor at 4 h. Their structures were determined by single-crystal X-ray diffraction methods in the cubic space group $Pm\bar{3}m$ (a=12.264(4) Å, a=12.269(1) Å, and a=12.332(3) Å, respectively) at 22(1)℃, and were refined to the final error indices, R(weighed), of 0.056 with 131 reflections, 0.068 with 108 reflections, and 0.070 with 94 reflections, respectively, for which $I>3\sigma(I)$. In these structures, Rb species are found at three different crystallographic sites; three Rb^+ ions per unit cell are located at 8-ring centers, ca. 6.0~6.8 Rb^+ ions are found opposite 6-rings on threefold axes in the large cavity, and ca. 2.5 Rb^+ ions are found on three fold axes in the sodalite unit. Also, Ag species are found at two different crystallographic sites; ca. 0.6~1.0 Ag^+ ion lies opposite 4-rings and about 1.8~4.2 Ag atoms are located near the center of the large cavity. In these structures, the numbers of Ag atoms per unit cell are 1.8, 3.0, and 4.2, respectively, and these are likely to form hexasilver clusters at the centers of the large cavities. The Rb^+ ions, by blocking 8-rings, may have prevented silver atoms from migrating out of the structure. Each hexasilver cluster is stabilized by coordination to 6-ring, 8-ring Rb^+ ions, and also by coordination to a 4-ring Ag^+ ion.

INTRODUCTION

Numerous investigations have been reported that various types of silver clusters are located in dehydrated fully and partially Ag^+ ion exchanged zeolite A, zeolite Y, mordenite, and chabazite[1~9]. The existences of these silver clusters were identified and reconfirmed by many workers using EPR spectroscopy[5,10~13], reflectance spectroscopy[14], and FTIR[15]. Ag^+ ions can be reduced by heating, and by reaction with reducing agents such as H_2 alcohol, and alkyl benzenes, or by the sorption of metal vapors[3,8]. In the structures of $Ag_{4.6}Na_{7.4}$-A dehydrated and treated with H_2 at 350℃, $(Ag_6)^{3+}$ clusters of low symmetry were found in the large cavity[3~9].

In the structure of fully Rb^+ ion exchanged zeolite A which was prepared by the sorption of rubidium metal vapor on dehydrated Na_{12}-A, Na^+ ions were reduced and replaced by Rb vapor and were found the large cavity to give an $(Rb_6)^{4+}$ cluster of symmetry $3m$ (C_{3v})[15]. Rb^+ ions, like Cs^+ ions, are large, monopositive, and exchanged only incompletely (about 90%) into zeolite A by flow method[16,17].

The neutrual cluster $(Ag_6)^0$, stabilized by coordination to 8 Ag^+ ions, has been found by X-ray diffraction method. This cluster may alternatively be viewed as $(Ag_{14})^{8+}$. Hermerschmidt and Haul also identified Ag_6^{n+} (n<6) clusters in the sodalite cavities of dehydrated Ag-A zeolite by EPR spectroscopy[10], and their results were duplicated by Grobet and Schoonheydt[11]. This was reverified by the careful work of Morton and Preston on Ag-A using isotopically pure silver[13]. Recently, fully Rb^+-exchanged zeolite A has been synthesized by the reduction of all Na^+ ions and Ca^{2+} ions in Na_{12}-A and Ca_4Na_4-A by rubidium vapor[14]. These redox reactions go to completion at 250℃ with ca. 0.1 torr of Rb^0. In these structures, extra Rb atoms are sorbed; these associate with Rb^+ ions to form $(Rb_6)^{4+}$, cationic clusters of symmetry $3m$ (C_{3v}).

This work was initiated with the expectation that the intrazeolitic redox potential for the reaction.

$$Ag_{12-x}Na_x\text{-A}+12Rb^0=Rb_{12}\text{-A}+(12-x)Ag^0+xNa^0$$

would be positive enough to ensure complete exchange. The E^0 values, not involving the zeolite, are easily calculated[18].

$$Rb(s)+Ag^+=Rb^++Ag^0(s) \quad E_{aq}^0=3.73\ V$$
$$Rb(s)+Na^+=Rb^++Na^0(s) \quad E_{aq}^0=0.19\ V$$

The resulting material would be interesting because the volume of exchangeable cations would be large and some extra Rb^0 atoms may be present, forming Rb clusters. However in this experiment, the reduced silver and sodium atoms may not be able to diffuse to the surface of zeolite because of the blockage of the 8-windows by the large Rb^+ ions. By such trapping, some new perhaps larger, clusters might form and can be identified. Furthermore, because of the atomic size and the high scattering powers of Rb^+ and Ag^+, precise and reliable crystallographic determinations should be easy to achieve.

EXPERIMENTAL SECTION

Complete Ag^+ exchange of zeolite 4A powder is accomplished by a static method: 0.2 grams of zeolite 4A (Union Carbide, Lot 494107701161) was allowed by exchange at 24℃ with 6-fold excess of 0.05N $AgNO_3$, and the solution was agitated periodically.

Each day, the supernatant solution was decanted and a fresh aliquot of 0.05 N $AgNO_3$ was added. After 7 days, the zeolite powder was filtered and dried. To prepare of $Ag_{12-x}Na_x$-A samples Ag_{12}-A and Na_{12}-A were mixed in 2.65 : 1, 4.60 : 1 and 6.25 : 1 weight ratio, respectively. A few large single crystals of zeolite 4A which had been prepared by Charnell's method[19] were added to these powder mixtures, with enough water to submerge all solid particles so that the composition of the large crystals would be $Ag_{12-x}Na_x$-A (x=4, 6 and 8) at equilibrium. After 3 days, the water was allowed to evaporate in air at room temperature.

A single crystal 0.08 mm on an edge was selected and lodged in a fine Pyrex capillary, The hydrated partially Ag^+-exchanged crystal was dehydrated for 48 h at 380℃ 2×10^{-6} torr. Rubidium vapor was introduced by distillation from a side-

arm break-seal ampule to the pyrex-tube extension of the crystal-containing capillary. This glass reaction vessel was then sealed off under vacuum and placed within a pair of cylindrical horizontal ovens, axes collinear attached. The oven about crystal always maintained at higher temperature than that about the rubidium metal so that rubidium would not distill onto the crystal.

The crystal, Rb(g) at 0.1 torr (the vapor pressure of Rb(l) at 220℃) was allowed to react with $Ag_{12-x}Na_x$-A at 250℃ for 4 h. Each crystal was then sealed off from its reaction vessel by torch after cooling to room temperature. Microscopic examination showed that all these crystals had become metallic black.

The space group $Pm\bar{3}m$ (no systematic absences) was used through this work for reasons discussed previously[20,21]. Preliminary crystallogrphic experiments and subsequent data collection were performed with a Enraf-Nonius 4-circle computer-controlled CAD-4 diffractometer, equipped with a graphite monochromator, a pulse-height analyzer, and Micro VAX 3100 computer. Molybdenum radiation ($K_{\alpha 1}$, $\lambda=0.70930$ Å, $K_{\alpha 2}$, $\lambda=0.71359$ Å) was used for all experiments. In each case, the cell constant, $a=12.264(4)$ Å, 12.269(1) Å, and 12.332(3) Å for crystals 1, 2, and 3, respectively, were determined by a least-squares treatment of 25 intense reflections for which $20°<2\theta<30°$.

Reflections from two intensity-equivalent regions of reciprocal space (hkl, $h\leq k\leq l$; hkl, $h\leq l\leq k$) were examined by using the $\omega-2\theta$ scan technique. The data were collected using variable scan speeds. Most reflections were observed at slow scan speeds, from 0.25 to 0.32 deg min^{-1} in ω. The intensities of three reflections in diverse regions of reciprocal space were recorded every 3 h to monitor crystal and instrument stability. Only small, random fluctuations of these check reflections were noted during the course of data collection. For each region of reciprocal space, the intensitities of all lattice points for which $2\theta<70°$ were recorded. The raw data from each region were corrected for Lorentz and polarization effects including beam monochromatization. The reduced intensities were merged, and the resultant estimated standard deviations were assigned to each averaged reflection by the computer programs, PAINT and WEIGHT[22]. Absorption corrections (μ_R ca. 0.38, 0.38 and 0.37) were jedged to be negligible for all crystals[23]. Of the 894, 896, and 880 pairs of reflections for crystal 1, 2, and 3, only the 131, 108, and 94 pairs, respectively, for which $I>3\sigma(I)$ were used in subsequent structure determinations.

STRUCTURE DETERMINATION

Crystal 1. (Dehydrated Ag_4Na_8-A treated with Rb(g)). Full-matrix least-squares refinement was initiated with atomic parameters of the framework atoms (Si, Al), O(1), O(2), and O(3) of dehydrated $Rb_{11}Na_1$-A[1].

Anisotropic refinement of the framework atoms converged to unweighted R_1 index, $(\sum||F_O|-|F_C||)/\sum F_O$, of 0.46 and a weighted R_2 index, $(\sum\omega(F_O-|F_C|)^2/\sum\omega F_O^2)^{1/2}$, of 0.55.

A subsequent Fourier synthesis revealed three large peaks at (0.0, 0.5, 0.5) of height 30.3(2) eÅ^{-3}, and (0.27, 0.27, 0.27) of height 46.9(3) eÅ^{-3}, and (0.10, 0.10, 0.10) of height 13.2(3) eÅ^{-3}.

Anisotropic refinement of the framework atoms and the Rb^+ ions at Rb(1), Rb(2), and Rb(3) (see *Table* 1(A)) converged $R_1=0.083$, and $R_2=0.071$ with occupancies 3.12(6), 6.57(8), 2.51(7) respectively. An ensuing differnece Fourier synthesis revealed the positions of Ag species at Ag(1), (0.255, 0.255, 0.5), with peak height 1.82(4) eÅ^{-3} and at Ag(2), (0.33, 0.5, 0.5) with peak height 5.72(4) eÅ^{-3}.

Ag(1) peak refined with an unusually large thermal parameter. Therefore, the isotropic thermal parameter of Ag(1) was fixed at the more resonable value given in *Table* 1(A). Allowing all occupancies of Rb(i), $i=1$, 2, and 3, and Ag(j), $j=1$ and 2, to vary, except that of Rb(1) which was not permitted to exceed 3.0 (its maximum occupancy by symmetry), and allowing all anisotropic thermal parameters to vary, except for that of Ag(1) which was refined isotropically, lead to $R_1=0.067$ and $R_2=0.056$ with refined occupancies as given in the last column of *Table* 1(A).

The largest peak on final difference Fourier function was at (0, 0, 0) with height 0.8(10) eÅ^{-3}.

Table 1. Positional, thermal, and occupancy parameters[a]

Atom	Wyc. Pos.	x	y	z	β_{11}[b] or B_{iso}[c]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy[d] Varied	Occupancy[d] Fixed
(A) Crystal 1 (Dehydrated Ag_4Na_8-A Treated with 0.1 torr of Rb vapor at 250℃ for 4 h)												
(Si, Al)	24(*k*)	0	1849(9)	3730(7)	32(6)	33(6)	7(5)	0	0	30(10)		24.0[e]
O(1)	12(*h*)	0	2290(30)	5000	90(30)	60(30)	20(20)	0	0	0		12.0
O(2)	12(*h*)	0	2910(20)	2910(20)	20(20)	40(20)	40(20)	0	0	20(50)		12.0
O(3)	24(*m*)	1150(10)	1150(10)	3460(20)	70(10)	70(10)	60(20)	90(10)	80(30)	80(30)		24.0
Rb(1)	3(*c*)	0	5000	5000	90(20)	180(10)	180(10)	0	0	0	3.00	
Rb(2)	8(*g*)	2677(5)	2677(5)	2677(5)	87(4)	87(4)	87(4)	80(10)	80(10)	80(10)	6.57(8)	
Rb(3)	8(*g*)	1060(10)	1060(10)	1060(10)	100(10)	100(10)	100(10)	20(30)	20(30)	20(30)	2.51(7)	
Ag(1)	12(*j*)	2400(10)	2400(10)	5000	7.0(Fixed)[f]						0.51(10)	
Ag(2)	6(*f*)	3360(60)	5000	5000	180(90)	250(70)	250(70)	0	0	0	1.67(7)	
(B) Crystal 2 (Dehydrated Ag_6Na_6-A treated with 0.1 torr of Rb vapor at 250℃ for 4 h)												
(Si, Al)	24(*k*)	0	1840(10)	3730(7)	44(8)	33(8)	10(6)	0	0	−0(2)		24.0[e]
O(1)	12(*h*)	0	2340(30)	5000	80(40)	10(30)	100(40)	0	0	0		12.0
O(2)	12(*h*)	0	2900(20)	2900(20)	30(30)	10(20)	10(20)	0	0	20(50)		12.0
O(3)	24(*m*)	1150(20)	1150(10)	3530(30)	60(10)	60(10)	100(40)	40(50)	40(40)	40(40)		24.0
Rb(1)	3(*c*)	0	5000	5000	100(20)	170(20)	170(20)	0	0	0	3.00	
Rb(2)	8(*g*)	2709(9)	2709(9)	2709(9)	115(6)	115(6)	115(6)	100(20)	100(20)	100(20)	5.80(10)	
Rb(3)	8(*g*)	1100(20)	1100(20)	1100(20)	90(10)	90(10)	90(10)	50(30)	50(30)	50(30)	2.64(6)	
Ag(1)	12(*j*)	2320(10)	2320(10)	5000	7.0(Fixed)[f]						0.84(10)	
Ag(2)	6(*f*)	3400(30)	5000	5000	150(40)	270(30)	270(30)	0	0	0	2.78(8)	
(C) Crystal 3 (Dehydrated Ag_8Na_4-A treated with 0.1 torr of Rb vapor at 250℃ for 4 h)												
(Si, Al)	24(*k*)	0	1820(10)	3730(10)	32(6)	33(6)	7(5)	0	0	30(10)		24.0[e]
O(1)	12(*h*)	0	2150(40)	5000	130(60)	70(30)	50(20)	0	0	0		12.0
O(2)	12(*h*)	0	2850(20)	2850(20)	80(40)	20(20)	20(20)	0	0	10(30)		12.0
O(3)	24(*m*)	1160(20)	1160(20)	3400(30)	120(2)	120(2)	100(30)	90(60)	−20(40)	−20(40)		24.0
Rb(1)	3(*c*)	0	5000	5000	170(10)	170(10)	170(10)	0	0	0	3.00	
Rb(2)	8(*g*)	2751(7)	2751(7)	2751(7)	64(9)	64(9)	64(9)	30(30)	30(30)	30(30)	6.19(12)	
Rb(3)	8(*g*)	1130(10)	1130(10)	1130(10)	110(5)	110(5)	110(5)	80(20)	80(20)	80(20)	2.61(10)	
Ag(1)	12(*j*)	2530(10)	2530(10)	5000	7.0(Fixed)[f]						0.66(8)	
Ag(2)	6(*f*)	3390(20)	5000	5000	230(40)	300(10)	300(10)	0	0	0	4.11(7)	

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

This peak was rejected because it was too close (2.25 Å) to Rb species at Rb(3).

Crystal 2. (Dehydrated Ag_6Na_6-A Treated with Rb(*g*)). Using the atomic coordinates from the structure of crystal 1, simultaneous occupancy, positional, and thermal parameter refinement was initiated. Anisotropic refinement of all positions, except for that of Ag(1), which was refined isotropically, converged quickly to $R_1=0.080$ and $R_2=0.065$. The number of Rb atoms and ions at Rb(1), Rb(2), Rb(3), Ag(1), and Ag(2) refined 3.06(3), 5.81(10), 2.64(6), 0.84(10), and 2.78(8) ions or atoms per unit cell, respectively. The occupancy of Rb(1) was fixed at 3.0 its maximum occupancy by symmetry. The final R values converged at $R_1=0.082$, and $R_2=0.068$.

A final difference Fourier synthesis was featureless except for some residual density (1.0(2) $eÅ^{-3}$) at (0.31, 0.5, 0.5) near Ag(2), deep in the large cavity.

Crystal 3. (Dehydrated Ag_8Na_4-A treated with Rb(*g*)). Using the atomic coordinates from the structure of crystal 1, simultaneous occupancy positional, and thermal parameter refinement was done. Anisotropic refinement for all positions, except for that of Ag(1), which was refined isotropically, converged to $R_1=0.075$ and $R_2=0.061$. Occupancy refinement converged 3.11(2), 6.19(12), 2.61(10), 0.66(8), and 4.11(7) for Rb(1), Rb(2), Rb(3), Ag(1), and Ag(2) (see *Table* 1(C)), respectively. The occupancy at Rb(1) was fixed at 3.0 as before. The final R values converged at $R_1=0.073$ and $R_2=0.063$.

The final difference Fourier function was featureless except for some residual density (0.9(3) $eÅ^{-3}$) at (0.31, 0.5, 0.5) near Ag(2), deep in the large cavity. All shifts in the final cycles of least-squares refinement for all three crystals were less than 0.1% of their corresponding standard deviations.

For all structures, the full-matrix least-squares program used minimized $\sum\omega(F_O-|F_C|)^2$; the weight ω of an observation was the reciprocal square of $\sigma(F)$, its standard deviation. Atomic scattering factors for Rb^+, Ag^+, Ag^0, O^- and $(Si, Al)^{+1.75}$ were used[24]. The function describing $(Si, Al)^{+1.75}$ is the mean of the Si^0, Si^{4+}, Al^0, and Al^{3+} functions. All scattering factors were modified to account for anomalous dispersion[25,26]. The final structure parameters and selected interatomic distances and angles are presencted in *Table* 1 and 2, respectively.

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

	Crystal 1	Crystal 2	Crystal 3
(Si, Al)-O(1)	1.64(1)	1.67(2)	1.60(2)
(Si, Al)-O(2)	1.66(2)	1.65(3)	1.66(3)
(Si, Al)-O(3)	1.64(4)	1.66(2)	1.69(2)
Rb(1)-O(1)	3.38(4)	3.27(4)	3.49(5)
Rb(1)-O(2)	3.61(1)	3.65(2)	3.77(2)
Rb(2)-O(2)	3.30(5)	3.34(1)	3.37(4)
Rb(2)-O(3)	2.81(1)	2.89(2)	2.87(2)
Rb(3)-O(2)	3.45(2)	3.39(2)	3.29(2)
Rb(3)-O(3)	2.94(3)	2.98(3)	2.78(3)
Ag(1)-O(1)	2.90(5)	2.84(5)	3.13(4)
Ag(1)-O(3)	2.83(7)	2.71(2)	3.09(2)
Ag(2)-O(1)	5.29(7)	5.29(4)	5.37(3)
Rb(1)-Rb(2)	5.19(5)	5.17(9)	5.15(2)
Rb(1)-Ag(1)	4.36(6)	4.34(7)	4.33(1)
Rb(2)-Rb(2)	5.50(3)	5.52(2)	5.51(1)
Rb(2)-Rb(3)	3.42(1)	3.41(1)	3.43(9)
Rb(3)-Rb(3)	4.52(1)	4.69(2)	4.84(1)
	3.82(1)	3.83(3)	3.91(5)
Ag(2)-Rb(1)	4.12(7)	4.17(4)	4.15(3)
Ag(2)-Rb(2)	4.00(2)	4.06(1)	3.97(5)
Ag(1)-Ag(2)	3.45(6)	3.54(1)	3.40(4)
Ag(2)-Ag(2)	2.85(7)	2.78(4)	2.78(9)
O(1)-(Si, Al)-O(2)	110.0(1)	107.0(2)	116.0(2)
O(1)-(Si, Al)-O(3)	111.0(9)	109.0(1)	111.0(1)
O(2)-(Si, Al)-O(3)	106.0(6)	108.1(9)	111.0(7)
O(3)-(Si, Al)-O(3)	112.1(7)	116.1(9)	114.1(4)
(Si, Al)-O(1)-(Si, Al)	143.0(2)	137.0(3)	151.0(3)
(Si, Al)-O(2)-(Si, Al)	167.0(2)	167.0(1)	161.0(2)
(Si, Al)-O(3)-(Si, Al)	145.0(2)	148.0(2)	139.2(1)
O(3)-Rb(2)-O(3)	90.1(4)	119.2(4)	119.3(3)
O(3)-Rb(2)-O(3)	87.0(4)	87.9(6)	88.6(5)
Ag(2)-Rb(1)-Ag(2)	180.0(1)	180.0(1)	180.0(0)

DISCUSSION OF STRUCTURE

In all three structures, Rb^+ ions are found at three different crystallographic sites. The three structure are similar except for the occupancies at the Rb(2), Rb(3), Ag(1), and Ag(2) positions.

In each structure, three Rb^+ ions at Rb(1) fill equipoints of symmetry C_{4h} (D_{4h} in $Pm\bar{3}m$) at the

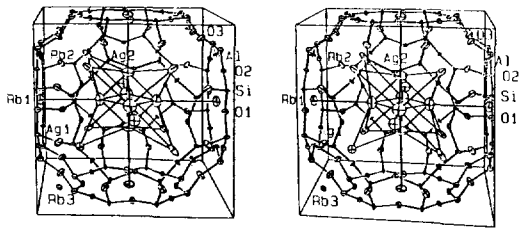

Fig. 1. A stereoview of the large cavity containing an Ag_6 molecule. The octahedral Ag_6 molecule, stabilized by coordination to 3 Rb^+ ions at Rb(1), 6 Rb^+ ions at Rb(2), 2 Rb species Rb(3) and one Ag^+ is shown. About 50% of the unit cells of crystal 2 and 3 may have this arrangement. Ellipsoids of 25% probability are used.

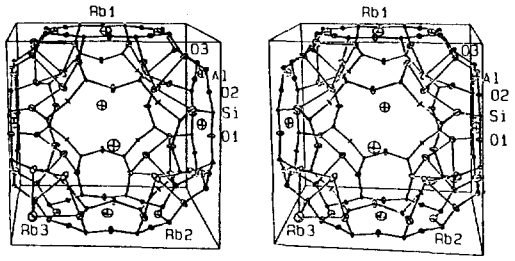

Fig. 2. A stereoview of the large cavity of dehydrated Ag_4Na_8-A treated with Rb vapor. 3 Rb^+ ions at Rb(1), 8 Rb^+ ions at Rb(2), 3 Rb species at Rb(3) are shown. About 40% of the unit cells may have this arrangement. Ellipsoids of 25% probability are used.

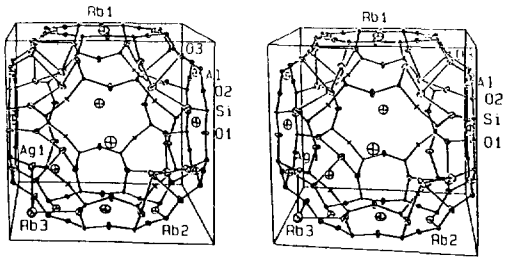

Fig. 3. A stereoview of the large cavity of dehydrated Ag_6Na_6-A treated with Rb vapor. 3 Rb^+ ions at Rb(1), 6 Rb^+ ions at Rb(2), 3 Rb species at Rb(3), and 1 Ag^+ at Ag(1) are shown. About 50% of the unit cells may have this arrangement. Ellipsoids of 25% probability are used.

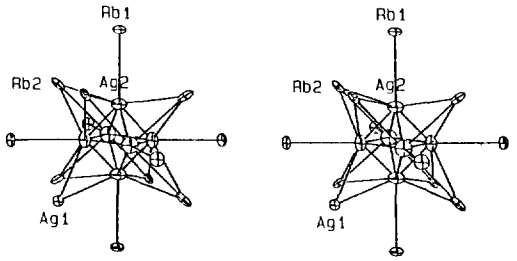

Fig. 4. The octahedral Ag_6 molecule, stabilized by coordination to 3 Rb^+ ions at Rb(1), 6 Rb^+ ions at Rb(2), and 1 Ag^+ ion is shown. Ellipsoids of 25% probability are used.

centers of 8-rings (see *Fig.* 1, 2, and 3).

Each Rb(1) ion is ca. 3.38(4) Å from four O(1) oxygens and ca. 3.66(1) 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 O^{2-} and Rb^+, 2.79 Å[26]. Rb^+ ions were observed at this site in all previous studies of Rb^+ exchanged zeolite A, with similar long contact distances[15~17].

In the large cavity opposite 6-ring, ca. 6.57(8), 5.80(10), and 6.19(7) Rb^+ ions are found at Rb(2) in crystal 1, 2, and 3, respectively. In the sodalite unit opposite 6-rings, 2.51(7), 2.64(6), and 2.61(10) Rb^+ ions, respectively, are found at Rb(3). The sum of these threefold-axis occupancies at Rb(2) and Rb(3) are 9.08, 8.45, and 8.80 for crystal 1, 2, and 3, respectively. If the Rb species at Rb(2) and Rb(3) are all ions, this sum should not exceed eight; otherwise an unacceptably short distance (3.42 Å) between Rb(2) and Rb(3) would exist. The distance of Rb(2)-Rb(3) is shorter ca. 1.0~0.5 than that of Rb(2)-Rb(3) contact distance. Also, the presence of more than two Rb(3) species per sodalite unit requires ca. 3.5 Å Rb(3)-Rb(3) contacts. Together, these observations indicate that the Rb species at Rb(3) must be partially reduced from Rb^+, to form, for example, $(Rb_3)^{2+}$ (*Fig.* 5). The short 3.41~3.43 Å distance that at least nearly one Rb^+ ion in this cluster must necessarily have with a large-cavity 6-ring Rb^+ ion indicates that it should instead be viewed as $(Rb_{n+1})^{n+}$, where n=3, 4, or 5.

It would consist of a central three-membered ring with one, two or three of the approximately six and/or eight Rb^+ ions in the large cavity included (*Fig* 1, 2, and 3). Each ion at Rb(2) is ca. 2.86 (2) Å from the three O(3) oxygens of its six-oxygen ring and ca. 1.67 Å from the (111) plane at

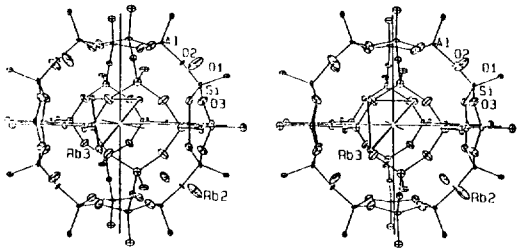

Fig. 5. Stereoview of a sodalite cavity. A $(Rb_3)^{2+}$ cluster is shown. Ellipsoids of 25% probability are used.

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

	Crystal 1	Crystal 2	Crystal 3
O(2)	−0.02(1)	−0.02(7)	−0.00(16)
Rb(2)	1.60(9)	1.62(7)	1.79(8)
Rb(3)	−1.81(5)	−1.78(1)	−1.64(10)
Ag(2)	5.38(4)	5.35(7)	5.43(3)

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

O(3). Rb(3) is correspondingly ca. 2.90(3) Å from three O(3) oxygens and recessed ca. 1.72 Å into sodalite cavity from the (111) plane of three O(3)'s (see *Table* 3).

In each structure, the Ag^+ ion at Ag(1) is statistically distributed over a 12-fold equipoint in the large cavity on a two fold axis opposite 4-ring (*Fig.* 1 and 2). This ion is rather far from framework oxygen Ag(1)-O(1)=ca. 2.96(5) Å and Ag(1)-O(3) =ca. 2.88(4) Å. Probably, because of an interaction with Ag(2) species. The other Ag position, Ag(2), is located near the center of the large cavity (*Fig.* 1 and 4) and is occupied by Ag atoms produced by the reduction of Ag^+ by Rb^0.

The sum of the Rb(*i*) and Ag(*j*) occupancies in crystal 1, 2, and 3 (see *Table* 1) are 14.2(6), 15.0(6), and 16.5(7), respectively. The unit cells clearly contain more metal species than the approximately 12 monovalent cations which are required to balance the anionic charge of the zeolite framework, which is estimated to be −11.75[27] to −12[21] per unit cell. Therefore ca. 2.0~4.5 metal atoms must exist per unit cell. Those may be present as isolated atoms or neutral clusters or they may associate with cations to form cationic clusters.

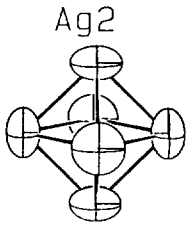

Fig. 6. The octahedral Ag_6 molecule is shown using ellipsoids of 50% probability.

The distance between Ag(2) and its nearest framework oxygens, four at O(1), is very much longer (Ag(2)-O(1)=ca. 5.33 Å) than the sum of the approximate ionic radii, 2.58 Å[26]. This indicates that the species at Ag(2) must be Ag^0 and not Ag^+. The shortest distance between Ag(2) and Ag(2), ca. 2.82 Å, which must exist whenever more than two silver species at Ag(2) are present per unit cell, is far too short to be an unmoderated Ag^+-Ag^+ distance. Crystal 2 and 3, at least, have more than two silver species at Ag(2). This Ag(2)-Ag(2) distance is close to Ag-Ag distance, 2.89 Å, in silver metal. If the Ag(2) equipoints were filled in fraction of the large cavities, closest packed clusters of six silver atoms would exist in all three structures. The hexasilver molecule would be octahedral and would show the full symmetry of its site, O_h, at center of the large cavity (*Fig.* 4 and 6).

The distances from Ag(2) to Rb(1) and Rb(2) are ca. 4.15 Å and 4.01 Å, respectively. These are almost the same as the sum of the van der Waals radius of Ag^0 and the ionic radius Rb^+, 1.34+2.80 =4.14 Å. The relatively large thermal ellipsoids of the Ag atoms at Ag(2) indicate that the hexasilver cluster is loosely held at its position.

To maximize the number of favorable interactions, each structure may be viewed as composed of several different unit cell compositions as *Table* 4. For example, about a half of the unit cell of crystal 2 may contain three Rb^+ ions at Rb(1), six Rb^+ ions at Rb(2), two Rb species at Rb(3), one Ag^+ ions at Ag(1), and six Ag atoms at Ag(2) (*Fig.* 1). The Ag atoms at Ag(2) would form a hexasilver cluster which would be stabilized by association with six ions at Rb(2) and three ions at Rb(1). Each of these latter Rb(1) ions is shared

Table 4. Inferred unit cell compositions for crystal 1, 2, and 3

Positions of cations and atoms	Crystal 1			Crystal 2			Crystal 3		
	40 %	30 %	30 %	50 %	50 %	10 %	20 %	20 %	50 %
8-ring, Rb(1)	3	3	3	3	3	3	3	3	3
6-ring, Rb(2)	8	6	6	6	6	8	6	6	6
6-ring, Rb(3)	3	2	2	3	2	3	3	3	2
Opposite 4-ring, Ag(1)	0	1	1	1	1	0	0	1	1
Center of large cavity, Ag(2)	0	0	6	0	6	0	0	6	6

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

by two clusters, so the formula of an individual metal cluster may be viewed as $(Ag^0)_6(Ag^+)(Rb^+)_9$ (*Fig.* 1 and 4). The remaining a half of the unit cell would have three Rb^+ ions at Rb(1), six Rb^+ ions at Rb(2), three species at Rb(3) and one Ag^+ ion at Ag(1) (*Fig.* 2).

Without a mechanism for their stabilization, metal clusters like hexasilver would generally not be retained within the the zeolite structure. Because a mechanism involving association with the ions at Rb(1) and Rb(2) is seen, it is reasonable to accept the fact that atoms of silver have formed and have been retained within zeolite A. A structure and symmetry of this hexasilver cluster is exactly the same that found at the center of sodalite unit in partially decomposed fully dehydrated Ag^+-exchanged zeolite A[2].

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