

750°C에서 탈수한 Cd₆-A의 결정구조와 이 결정을 세슘 증기로 반응시킨 결정구조

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Crystal Structures of Cd₆-A Dehydrated at 750°C and Dehydrated Cd₆-A Reacted with Cs Vapor

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요 약. Cd²⁺ 이온으로 이온 교환된 제올라이트 A를 750°C에서 2×10^{-6} torr의 진공하에서 탈수한 구조 ($a=12.204(1)$ Å)와 이 결정에 250°C에서 12시간동안 약 0.1 torr의 Cs 증기로 반응시킨 구조 ($a=12.279(1)$ Å)를 21°C에서 입방공간군 $Pm\bar{3}m$ 를 사용하여 단결정 X-선 회절법으로 해석하고 정밀화하였다. 탈수한 Cd₆-A의 구조는 Full-matrix 최소자승법 정밀화 계산에서 $I > 3\sigma(I)$ 인 151개의 독립반사를 사용하여 최종 오차 인자를 $R_1=0.081$, $R_2=0.091$ 까지 정밀화 계산하였고, 이 결정을 세슘 증기로 반응시킨 구조는 82개의 독립반사를 사용하여 $R_1=0.095$, $R_2=0.089$ 까지 각각 정밀화시켰다. 탈수한 Cd₆-A의 구조에서는 단위세포당 6개의 Cd²⁺ 이온은 O(3)의 (111) 평면에서 소다라이트 동공쪽으로 약 0.460 Å 들어간 자리에 위치하였다 (Cd-O(3)=2.18(2) Å, O(3)-Cd-O(3)=115.7(4)°). 또 약 0.1 torr의 Cs 증기를 써서 250°C에서 반응시킨 결정에서는 탈수한 Cd₆-A의 6개의 Cd²⁺ 이온은 모두 Cs 증기에 의해 환원되고 세슘은 4개의 다른 결정학적 자리에 위치하였다. 3개의 Cs⁺ 이온은 D_{4h}의 대칭을 가지고 8-링의 중심에 위치하였다. 단위세포당 약 9개의 Cs⁺ 이온은 3회 회전축상에 위치하였다. 그 중 약 7개의 Cs⁺ 이온은 큰 동공내의 3회 회전축상의 6-링에 위치하고 2개의 Cs⁺ 이온은 소다라이트 동공내에 존재한다. 0.5개의 Cs⁺ 이온은 큰 동공의 4-링과 마주보는 위치에 위치한다. 이 구조에서 제올라이트 골조의 음하전을 상쇄시키는데 필요한 단위세포당 12개의 Cs⁺ 이온보다 많은 약 12.5개의 Cs 종이 존재한다. 즉 Cs⁰가 흡착 되었음을 알 수 있다. 또 관측한 점유수에서 두 종류의 단위 세포 배열 즉 Cs₁₂-A와 Cs₁₃-A가 존재함을 알 수 있다. 단위세포의 약 50%는 2개의 Cs⁺ 이온이 소다라이트 동공내에서 6-링 가까이 존재하고 6개의 Cs⁺ 이온은 큰 동공내에서 6-링 가까이 위치한다. 1개의 Cs⁺ 이온은 큰 동공내에서 4-링과 마주보는 위치에 있다. 단위세포의 나머지 50%는 소다라이트 동공내에 2개의 Cs 종이 위치하고 큰 동공내에 있는 8개의 Cs⁺ 이온 중 2개의 Cs⁺ 이온과 결합하여 선형의 (Cs₂)⁺ 클러스터를 형성하고 있다. 이 클러스터는 3회 회전축상에 놓여있고 소다라이트 동공 중심을 지나가고 있다. 모든 단위세포는 3개의 Cs⁺ 이온이 D_{4h}의 대칭을 가지고 8-링 중심에 위치하고 있다.

ABSTRACT. The crystal structures of Cd₆-A evacuated at 2×10^{-6} torr and 750°C ($a=12.204(1)$ Å) and dehydrated Cd₆-A reacted with 0.1 torr of Cs vapor at 250°C for 12 hours ($a=12.279(1)$ Å) have been determined by single crystal X-ray diffraction techniques in the cubic space group $Pm\bar{3}m$ at 21(1)°C. Their structures were refined to final error indices, $R_1=0.081$ and $R_2=0.091$ with 151 reflections and $R_1=0.095$ and $R_2=0.089$ with 82 reflections, respectively, for which $I > 3\sigma(I)$. In vacuum dehydrated Cd₆-A, six Cd²⁺ ions occupy threefold-axis positions near 6-ring, recessed 0.460(3) Å into the sodalite cavity from the (111) plane at O(3): Cd-O(3)=2.18(2) Å and O(3)-Cd-O(3)=115.7(4)°. Upon treating it with

0.1 torr of Cs vapor at 250°C, all 6 Cd^{2+} ions in dehydrated $\text{Cd}_6\text{-A}$ are reduced by Cs vapor and Cs species are found at 4 crystallographic sites: 3.0 Cs^+ ions lie at the centers of the 8-rings at sites of D_{4h} symmetry; ca. 9.0 Cs^+ ions lie on the threefold axes of unit cell, ca. 7 in the large cavity and ca. 2 in the sodalite cavity; ca. 0.5 Cs^+ ion is found near a 4-ring. In this structure, ca. 12.5 Cs species are found per unit cell, more than the twelve Cs^+ ions needed to balance the anionic charge of zeolite framework, indicating that sorption of Cs^0 has occurred. The occupancies observed are simply explained by two unit cell arrangements, $\text{Cs}_{12}\text{-A}$ and $\text{Cs}_{13}\text{-A}$. About 50% of unit cells may have two Cs^+ ions in sodalite unit near opposite 6-rings, six in the large cavity near 6-ring and one in the large cavity near a 4-ring. The remaining 50% of unit cells may have two Cs species in the sodalite unit which are closely associated with two out of 8 Cs^+ ions in the large cavity to form linear $(\text{Cs}_4)^{3+}$ clusters. These clusters lie on threefold axes and extend through the centers of sodalite units. In all unit cells, three Cs^+ ions fill equipoints of symmetry D_{4h} at the centers of 8-rings.

INTRODUCTION

Complete dehydration of fully Cd^{2+} -exchanged zeolite A has not been achieved. $\text{Cd}_6\text{-A}$ evacuated at 500°C and 10^{-6} torr for 2 days contains three H_2O molecules per unit cell^{1,2}, and temperatures as high as 700°C have not been sufficient to remove all of them³.

In 1987, Seff and Heo succeeded in preparing fully dehydrated, fully Cs^+ -exchanged zeolite A by the reduction of all Na^+ ions in $\text{Na}_{12}\text{-A}$ with cesium vapor⁴. The redox reaction goes to completion at 350°C with 0.1 torr of Cs^0 to give $\text{Cs}_{12}\text{-A}\cdot 1/2\text{Cs}$. In this structure, each extra Cs atom associates with two or three Cs^+ ions to form linear $(\text{Cs}_3)^{2+}$ or $(\text{Cs}_4)^{3+}$ clusters. Complete reactions of Na^+ , K^+ and Co^{2+} ions in dehydrated zeolite A with Cs vapor are readily achieved at 250°C or higher^{5,6}. The Ca^{2+} ions in fully dehydrated fully Ca^{2+} -exchanged zeolite A were reduced by cesium vapor. However the reaction products had a different degree of Cs^+ compositions in zeolite A unit cell. The extent of reaction depended upon experimental conditions⁶. Even though divalent cation forms of zeolite A have only six exchangeable cations per unit cell, it appears that they present a different degree of window blocking and different electrostatic barrier in the channels and cavities to the cations that must migrate for the observed redox reaction to occur. When dehydrated $\text{Ag}_{12}\text{-A}$ was exposed to ca. 0.1 torr of Cs vapor at 220°C, the resulting crystal showed no single-crystal diffraction pattern, indicating that

the crystallinity of the zeolite A structure had been lost⁷.

This work was initiated to investigate the Cd^{2+} positions in the crystal structure of the fully dehydrated fully Cd^{2+} -exchanged zeolite A. This work was also done to learn about Cs^+ positions and the structure of interesting cesium clusters in the crystal structure of fully dehydrated $\text{Cd}_6\text{-A}$ reacted with Cs vapor.

EXPERIMENTAL SECTION

Crystals of zeolite 4A were prepared by a modification of Charnell's method⁸. Each of two single crystals about 85 μm on an edge was selected and lodged in a fine quartz capillary. An exchange solution of $\text{Cd}(\text{NO}_3)_2$ and $\text{Cd}(\text{OOCCH}_3)_2$ in the mole fraction of 1:1 with a total concentration 0.05 *M* was allowed to flow past each crystal at a velocity of approximately 1.5 cm/sec for 3 days. Each crystal was washed for 1 hr with distilled water at 80°C.

Each crystal, placed in a finely drawn quartz capillary, was attached to a vacuum system and cautiously dehydrated by gradually increasing its temperature (ca. 25°/hr) to 750°C at a constant pressure of 2×10^{-6} torr. Finally, the system was maintained at the state for 48 hrs. After cooling to room temperature, one crystal (crystal 1), still under vacuum, was sealed in its capillary by torch. Both crystals were colorless. Cesium vapor was introduced by distillation from a side-arm break-seal ampule to the glass-tube extension of the cr-

ystal-containing capillary. The glass reaction vessel was then sealed off under vacuum and placed within a pair of cylindrical horizontal oven, axis colinear, attached. The oven about the crystal was always maintained at a higher temperature than that about the cesium metal so that cesium would not distill onto the crystal. The crystal was allowed to react with 0.1 torr of Cs vapor at 250°C for 12 hours, after which it was sealed off from the reaction vessel by torch after cooling to room temperature. Microscopic examination showed that the crystal (crystal 2) had become black.

X-RAY DATA COLLECTION

The cubic space group *Pm3m* (no systematic absences) was used instead of *Fm3c* throughout this work for the reasons discussed previously by Seff and Mellum^{10,11}. Diffraction data were collected with an automated Enraf-Nonius four-circle computer controlled CAD-4 diffractometer equipped with a pulse-height analyzer and a graphite monochromator, using Mo K α radiation ($K\alpha_1$, $\lambda=0.70930$ Å, $K\alpha_2$, $\lambda=0.71359$ 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 $a=12.204(1)$ Å for Cd₆-A and $a=12.279(1)$ Å for Cs_{12.7}-A, 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 -2 θ 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 0.32° 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 and X-ray source stability. Only small, random fluctuations of these check reflections were noted during the course of data collections. For each region of reciprocal space, the intensities of all lattice points for which $2\theta < 70^\circ$ and $2\theta < 60^\circ$ were recorded, respectively. Only those of which $I > 3\sigma(I)$ were used for structure solution and refine-

ment. These amounted to 151 of the 862 reflections examined for the crystal 1, and 82 of the 605 reflections for crystal 2, respectively.

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 WEI-GHT¹².

An absorption correction ($\mu R=0.090$, $\rho_{cal}=1.408$ g/cm³ and $F(000)=990$ for the first crystal, and $\mu R=0.298$, $\rho_{cal}=2.875$ g/cm³ and $F(000)=1412$ for the second crystal) was judged to be negligible and was not applied¹³.

STRUCTURE DETERMINATION

Dehydrated Cd₆-A at 750°C. Full-matrix least-squares refinement was initiated by using the atomic parameters of the framework atoms [(Si, Al), O(1), O(2), and O(3)] of vacuum dehydrated Cd₆-A at 450°C¹⁴. Anisotropic refinement of the framework atoms converged to an R_1 index, $(\sum |F_o - |F_c||) / \sum F_o$ of 0.451 and a weighted R_2 index, $(\sum w(F_o - |F_c|)^2 / \sum w F_o^2)^{1/2}$ of 0.542.

The initial difference Fourier function revealed one large peak at (0.166, 0.166, 0.166) of height of 13.40(19) eÅ⁻³. This peak was stable at least-squares refinement. Anisotropic refinement of the framework atoms and isotropic refinement of the Cd²⁺ ions lowered the error indices to $R_1=0.117$ and $R_2=0.112$.

The occupancy number of Cd²⁺ ions per unit cell was refined to Cd=6.28(11). This was fixed at Cd=6.0 because the cationic charge should not be exceeded +12 per *Pm3m* unit cell. Anisotropic refinement of the framework atoms and Cd²⁺ ions converged to $R_1=0.081$ and $R_2=0.091$ (see Table 1). In the final cycle of least-squares refinement, all shifts in atomic parameters were less than 0.3 % of their corresponding standard deviations. The final difference function was featureless except one at (0.0, 0.0, 0.0) with peak height of 2.3(16) eÅ⁻³. This peak was not refined at the least-squares refinement.

Dehydrated Cd₆-A at 750°C treated with 0.1 torr

Table 1. Positional, thermal, and occupancy parameters^a
Crystal 1. Dehydrated Cd₆-A at 750°C

Atom	Wyckoff position	x	y	z	β_{ij} ^b						Occupancy ^c	
					β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	varied	fixed
(Si, Al)	24(k)	0	1836(8)	3690(8)	33(6)	40(7)	39(6)	0	0	10(10)	24.0 ^d	
O(1)	12(h)	0	2020(20)	5000	70(30)	30(30)	40(20)	0	0	0	12.0	
O(2)	12(i)	0	2960(20)	2960(20)	80(30)	40(10)	40(10)	0	0	100(40)	12.0	
O(3)	24(m)	1120(10)	1120(10)	3260(20)	50(10)	50(10)	90(20)	30(30)	30(30)	30(30)	24.0	
Cd	8(g)	1619(4)	1619(4)	1619(4)	116(2)	116(2)	116(2)	186(6)	186(6)	186(6)	6.28(11)	6.0

Crystal 2. Dehydrated Cd₆-A treated with 0.1 torr of Cs vapor at 250°C for 12 hrs

Atom	Wyckoff position	x	y	z	β_{ij} ^b						Occupancy ^c	
					β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	varied	fixed
(Si, Al)	24(k)	0	1820(20)	3760(20)	60(20)	40(20)	40(20)	0	0	60(50)	24.0 ^d	
O(1)	12(h)	0	2250(70)	5000	100(80)	130(90)	-20(50)	0	0	0	12.0	
O(2)	12(i)	0	2980(40)	2980(40)	-20(50)	130(60)	130(60)	0	0	-200(200)	12.0	
O(3)	24(m)	1090(30)	1090(30)	3600(60)	90(30)	90(30)	160(70)	100(100)	-0(100)	-0(100)	24.0	
Cs(1)	3(c)	0	5000	5000	230(40)	80(10)	80(10)	0	0	0	3.24(10)	3.0
Cs(2)	8(g)	2798(7)	1978(7)	2978(7)	101(5)	101(5)	101(5)	10(20)	10(20)	10(20)	6.83(12)	7.0
Cs(3)	8(g)	1070(20)	1070(20)	1070(20)	50(20)	50(20)	50(20)	-80(40)	-80(40)	-80(40)	2.29(14)	2.0
Cs(4)	12(j)	2500(100)	2500(100)	5000	4(6) ^e						0.55(15)	0.5

^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 are given as the number of atoms or ions per unit cell. ^dOccupancy for (Si) = 12; occupancy for (Al) = 12. ^eIsotropic thermal parameter in units \AA^2 .

Cs vapor at 250°C for 12 hrs. 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 Ag₂Cs₁₀-A¹⁵. Anisotropic refinement of the framework atoms converged to an R_1 index of 0.495 and a weighted R_2 index of 0.524.

An initial Fourier synthesis revealed three large peaks at (0,0, 0.5, 0.5) of peak height 37.7(5) $\text{e}\text{\AA}^{-3}$, (0.275, 0.275, 0.275) of peak height 49.8(3) $\text{e}\text{\AA}^{-3}$, and (0.107, 0.107, 0.107) of peak height 18.3(3) $\text{e}\text{\AA}^{-3}$. Anisotropic refinement of the framework atoms and the Cs⁺ ions at Cs(1), Cs(2), and Cs(3) converged to $R_1=0.102$ and $R_2=0.099$ with occupancies of 3.24(10), 6.83(12), and 2.29(14), respectively (see Table 1).

A subsequent difference Fourier synthesis revealed a peak of height 2.7(2) $\text{e}\text{\AA}^{-3}$ at (0.255, 0.255, 0.5). This peak refined with an unusually large thermal parameter. Therefore, the isotropic ther-

mal parameter of Cs(4) was fixed at the more reasonable value given in Table 1. Allowing all occupancies of Cs(*i*), *i* = 1~4 to vary except that at Cs(1), which was not permitted to exceed 3.0 (its maximum occupancy by symmetry), led to $R_1=0.099$ and $R_2=0.088$. A unit cell with a Cs⁺ ion at Cs(4) can not have more than 6 Cs⁺ ions at Cs(2) because otherwise there must be a very short Cs(2)-Cs(4) interaction (Cs(2)-Cs(4) = 2.76(2) \AA). Then the other half of the unit cell must have 8 Cs⁺ ion Cs(2) and no Cs⁺ ion at Cs(4). Therefore, the occupancy numbers of Cs(*i*), *i* = 1, 2, 3, and 4, were reset and fixed within their 2.5 esd's as in the last column of Table 1. The final error indices converged to $R_1=0.095$ and $R_2=0.089$. The final difference function was featureless except for one at the origin of height 2.6(10) $\text{e}\text{\AA}^{-3}$.

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

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

	Crystal 1	Crystal 2
(Si, Al)-O(1)	1.61(1)	1.61(4)
(Si, Al)-O(2)	1.64(2)	1.71(4)
(Si, Al)-O(3)	1.71(1)	1.62(3)
Cd-O(3)	2.18(2)	
Cs(1)-O(1)		3.38(8)
Cs(1)-O(2)		3.51(3)
Cs(2)-O(3)		3.13(3)
Cs(3)-O(3)		3.10(7)
Cs(4)-O(1)		3.05(2)
Cs(4)-O(3)		3.00(10)
Cs(1)-Cs(2)		5.14(1)
Cs(1)-Cs(4)		4.30(10)
Cs(2)-Cs(2)		5.41(2)
Cs(2)-Cs(3)		3.67(1)
Cs(2)-Cs(4)		2.76(2)
Cs(3)-Cs(3)		4.57(2)
O(1)-(Si, Al)-O(2)	115(1)	105(3)
O(1)-(Si, Al)-O(3)	111.9(9)	107(3)
O(2)-(Si, Al)-O(3)	105.3(6)	113(2)
O(3)-(Si, Al)-O(3)	102.0(7)	111(2)
(Si, Al)-O(1)-(Si, Al)	164(2)	142(6)
(Si, Al)-O(2)-(Si, Al)	156(1)	157(2)
(Si, Al)-O(3)-(Si, Al)	137(1)	154(4)
O(3)-Cd-O(3)	115.7(4)	
O(3)-Cs(2)-O(3)		88(4)
O(3)-Cs(3)-O(3)		88.4(4)
Cs(2)-Cs(3)-Cs(3)		180

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

of $\sigma(F_o)$, its standard deviation. Atomic scattering factors^{16,17} for Cd²⁺, Cs⁺, 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 correction¹⁸. The final structural parameters and selected interatomic distances and angles are presented in Table 1 and 2, respectively.

DISCUSSION

In the crystal structure of vacuum dehydrated

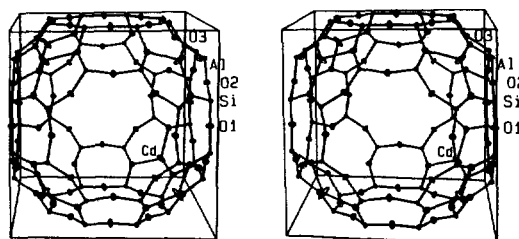


Fig. 1. A stereoview of large cavity of vacuum dehydrated Cd₆-A at 750°C. Six Cd²⁺ ions at Cd is shown. Ellipsoids of 20% probability are used.

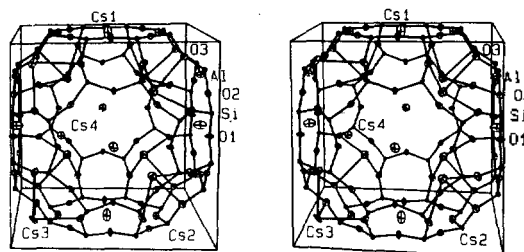


Fig. 2. A stereoview of a large cavity in Cs₁₂-A. Six Cs⁺ ions at Cs(2), two Cs⁺ ions at Cs(3), three Cs⁺ ions at Cs(1), and one Cs⁺ ion at Cs(4) are shown. About 50% of the large cavities may have this arrangement. Ellipsoids of 20% probability are used.

Cd₆-A, all six Cd²⁺ ions occupy threefold-axis positions near 6-ring, recessed 0.460(3) Å into the sodalite cavity from the (111) plane at O(3) (see Fig. 1). Each of these Cd²⁺ ions is coordinated to three O(3) framework oxygens at 2.18(2) Å. For comparison, the sum of the conventional ionic radii of Cd²⁺ and O²⁻ is 2.29 Å⁸. The angle of O(3)-Cd-O(3) has 115.7(4)°, close to the trigonal planar angle (see Table 2 and Fig. 1).

Upon treating dehydrated Cd₆-A with 0.1 torr of Cs vapor at 250°C, all six Cd²⁺ ions in Cd₆-A are reduced by Cs vapor and Cs atoms are oxidized. Cs⁺ ions are found at four crystallographic sites (see Table 1). 7.0 Cs⁺ ions at Cs(2) are on threefold axes in the large cavity. Each of these extends 1.858(5) Å into the large cavity from the (111) plane at O(3) and coordinates to three O(3) oxygens of the 6-ring at 3.13(3) Å. 2.0 Cs⁺ ions at Cs(3) are also on threefold axes and associate with 6-rings, but they are recessed 1.809(12) Å into the sodalite cavity from the (111) plane

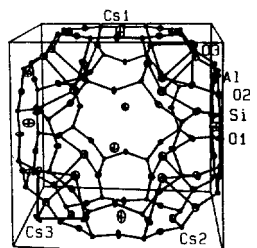
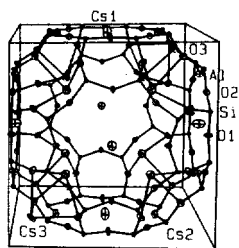


Fig. 3. A stereoview of a large cavity in $Cs_{13}\text{-A}$. Eight Cs^+ ions at Cs(2), two Cs^+ ions at Cs(3), and three Cs^+ ions at Cs(1) are shown. About 50% of the large cavities may have this arrangement. Ellipsoids of 20% probability are used.

at O(3). Each of these ions coordinates to three O(3) oxygens at 3.10(7) Å (see Fig. 2 and 3). The sum of the occupancies of Cs species on the threefold axes is ca. 9.0(2).

The product crystal, $Cs_{12.5}\text{-A}$, contains more Cs species than are required to balance the anionic charge of the zeolite framework, which is variously estimated to be -11.75^{19} to -12^{10} . Therefore about 1/2 Cs species is too many in $Cs_{12.5}\text{-A}$ and this excess is attributed to cesium atom sorption.

The fractional occupancy at Cs(4) indicates the existence of two types of unit cells, $Cs_{12}\text{-A}$ and $Cs_{13}\text{-A}$. In $Cs_{12}\text{-A}$, two adjacent 6-rings in each large cavity are occupied by sodalite-unit Cs^+ ions, allowing one Cs^+ ion to be in the large cavity, at Cs(4), opposite the 4-ring which connects those two 6-rings. Six large cavity Cs^+ ions fill the remaining six-ring. In $Cs_{13}\text{-A}$, all eight threefold axis sites in the large cavity are occupied by Cs^+ ions, so no 4-ring site is available. Two opposite 6-ring sites in the sodalite cavity are occupied by Cs species (because there is no way that Cs(2) and Cs(3) can avoid each other, this unit cell must have $(Cs_4)^{3+}$ cluster). All unit cells have 3 Cs^+ ions at Cs(1).

$Cs_{13}\text{-A}$ may be viewed as a material with 12.0 Cs^+ ions and one Cs atom. Sodalite unit with two Cs(3)'s must have Cs(3)-Cs(3) distance of 4.57(2) Å. This distance is quite short as compared to the bond length in Cs metal, 5.31 Å. Each Cs(3) species in the sodalite unit is better associated with one Cs(2) in the large cavity to allow electron

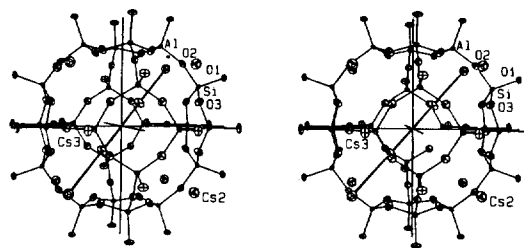


Fig. 4. A stereoview of a sodalite cavities of $Cs_{13}\text{-A}$. A linear $(Cs_4)^{3+}$ cluster is shown. About 50% of sodalite units may have this arrangement. Ellipsoids of 20% probability are used.

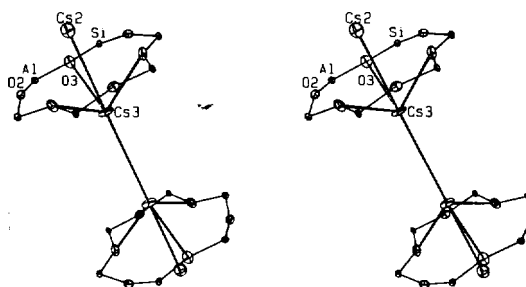


Fig. 5. A close up stereoview of linear cesium cluster, $(Cs_4)^{3+}$, on a threefold axis passing through the sodalite cavity of $Cs_{13}\text{-A}$. Ellipsoids of 20% probability are used.

delocalization (Cs(2)-Cs(3)) = 3.67(1) Å. Thus, these Cs species are associated with each other to form linear $(Cs_4)^{3+}$ cations. $(Cs_4)^{3+}$ clusters lie on threefold axes and extend through the center of sodalite unit. Linear $(Cs_4)^{3+}$ clusters are also found in the structure of dehydrated $Na_{12}\text{-A}$ reacting with cesium vapor⁵. These $(Cs_4)^{3+}$ clusters form a linear array with intercesium distances of 3.67, 4.57, and 3.67 Å. These are shorter than or comparable to those in Cs metal, 5.31 Å. $(Cs_4)^{3+}$ can be viewed as a one-dimensional particle-in-a-box: four linear arranged Cs^+ ion with one electron delocalized among them. The length of the box, ca. 15.25 Å is approximated by the sum of the three bond lengths plus twice the ionic radius of Cs^+ . A broad absorption transition (1 → 4) is allowed near the middle of the visible range at about 5115 Å, which could account for the black color of the $(Cs_4)^{3+}$ containing crystal.

Three Cs^+ ions at Cs(1) fill the equipoints of

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

	Crystal 1	Crystal 2
O(2)	0.294(12)	0.135(27)
Cd	-0.460(3)	
Cs(2)		1.858(5)
Cs(3)		-1.809(12)

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

symmetry C_{4h} (C_{4h} in $Pm3m$) at the centers of the 8-rings (see Fig. 2 and 3), as they have in all previously reported Cs⁺-exchanged zeolite A structures²⁰⁻²⁵. Each Cs(1) cation is 3.38(8) Å from four O(1) oxygens and 3.51(3) 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 Cs⁺, 2.99 Å. Theoretical calculations support this observation of a potential energy minimum at these positions^{26,27}.

The Cs⁺ ion at Cs(4) lies opposite a 4-ring. This Cs⁺ ion is rather far from the framework oxygens (ca. 3.05 Å from O(1) and 3.00(10) Å from O(3), perhaps because of repulsive interactions with the Cs⁺ ions on the sodalite unit site of in the adjacent 6-ring). This distance may be virtual, a bit too long; this particular 4-ring may be distorted from the mean 4-ring geometry due to the presence of its Cs⁺ ion. It is clear by its low occupancy that Cs(4) is energetically the least favorable Cs⁺ site.

During this work, another crystal was prepared by an identical procedure, except for the dehydration step; the crystal is dehydrated at 450°C for two days. The resulted crystal showed no single-crystal diffraction pattern. According to previous works, the crystal which was dehydrated at 500°C for two days must have three water molecules per unit cell². These water molecules react with Cs vapor and Cd²⁺ ions at 250°C, and may produce Cd⁰, Cs⁺, cesium cation clusters, H⁺, and OH⁻ ions. The resulted H⁺ ions attacked framework oxygens and apparently destroyed framework. However, the present crystal showed good single-crystal diffraction pattern, indicating that

Cd₆-A should be fully dehydrated at 750°C and $P=2 \times 10^{-6}$ torr for two days. The distance between Cd²⁺ and O(3) in the present work is 2.18(2) Å and that in partially dehydrated Cd₆-A is 2.23(1) Å, indicating that Cd²⁺ ions of the present crystal are firmly held by framework oxygens.

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