Crystal Structures of Cd$_6$A Dehydrated at 750°C and Dehydrated Cd$_6$A Reacted with Cs Vapor

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ABSTRACT. The crystal structures of Cd$_6$A evacuated at 2×10$^{-8}$torr and 750°C (α=12.204(1) Å) and dehydrated Cd$_6$A reacted with 0.1 torr of Cs vapor at 250°C for 12 hours (α=12.279(1) Å) have been determined by single crystal X-ray diffraction techniques in the cubic space group $Pm3m$ at 211°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 $I>3σ(I)$. In vacuum dehydrated Cd$_6$A, six Cd$^{2+}$ 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

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INTRODUCTION

Complete dehydration of fully Cd\textsuperscript{2+}-exchanged zeolite A has not been achieved. Cd\textsubscript{6}A evacuated at 500°C and 10\textsuperscript{4} torr for 2 days contains three H\textsubscript{2}O molecules per unit cell\textsuperscript{1,2}, and temperatures as high as 700°C have not been sufficient to remove all of them\textsuperscript{3}.

In 1987, Seff and Heo succeeded in preparing fully dehydrated, fully Cs\textsuperscript{+}-exchanged zeolite A by the reduction of all Na\textsuperscript{+} ions in Na\textsubscript{12}A with cesium vapor\textsuperscript{4}. The redox reaction goes to completion at 350°C with 0.1 torr of Cs\textsuperscript{+} to give Cs\textsubscript{12}-A/1/2Cs. In this structure, each extra Cs atom associates with two or three Cs\textsuperscript{+} ions to form linear (Cs\textsubscript{2})\textsuperscript{4+} or (Cs\textsubscript{4})\textsuperscript{2+} clusters. Complete reactions of Na\textsuperscript{+}, K\textsuperscript{+} and Cd\textsuperscript{2+} ions in dehydrated zeolite A with Cs vapor are readily achieved at 250°C or higher\textsuperscript{5,6}. The Ca\textsuperscript{2+} ions in fully dehydrated fully Ca\textsuperscript{2+}-exchanged zeolite A were reduced by cesium vapor. However, the reaction products had a different degree of Cs\textsuperscript{+} compositions in zeolite A unit cell. The extent of reaction depended upon experimental conditions\textsuperscript{7}. 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 Ag\textsubscript{12}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 lost\textsuperscript{8}.

This work was initiated to investigate the Cd\textsuperscript{2+} positions in the crystal structure of the fully dehydrated fully Cd\textsuperscript{2+}-exchanged zeolite A. This work was also done to learn about Cs\textsuperscript{+} positions and the structure of interesting cesium clusters in the crystal structure of fully dehydrated Cd\textsubscript{6}A reacted with Cs vapor.

EXPERIMENTAL SECTION

Crystals of zeolite 4A were prepared by a modification of Charnell's method\textsuperscript{9}. Each of two single crystals about 85 μm on an edge was selected and lodged in a fine quartz capillary. An exchange solution of Cd(NO\textsubscript{3})\textsubscript{2} and Cd(OOCCH\textsubscript{3})\textsubscript{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\textsuperscript{-4} 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-

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crystal-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 Seif and Mellum.\cite{SeifMellum1991} 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 Kα radiation (Kα1, \(λ = 0.70930\) Å, Kα2, \(λ = 0.71359\) Å). In each case, the unit cell constants at 21(1)° determined by least squares refinement of 25 intense reflections for which 18°<2θ<25° are \(a = 12.204(1)\) Å for Cd4-A and \(a = 12.279(1)\) Å for Cs2-A, respectively.

For each crystal, reflections from two intensity-equivalent regions of reciprocal space \((hkl, h\leq k \leq l\) and \(1hk, l\leq h\leq k)\) were examined. The intensities were measured using \(ω-2θ\) scan technique over a scan width of \((0.80 + 0.344 \tan θ)°\) 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 2θ<70° and 2θ<60° were recorded, respectively. Only those of which \(I > 3σ(I)\) were used for structure solution and refinement. 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 WIGHT\textsuperscript{12}.

An absorption correction (\(μR = 0.090, ρ_{abs} = 1.408\) g/cm\(^3\) and \(F(000)=990\) for the first crystal, and \(μR = 0.298, ρ_{abs} = 2.875\) g/cm\(^3\) and \(F(000)=1412\) for the second crystal) was judged to be negligible and was not applied\textsuperscript{12}.

STRUCTURE DETERMINATION

Dehydrated Cd4-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 Cd4-A at 450°C.\cite{SeifMellum1991} Anisotropic refinement of the framework atoms converged to an \(R_1\) index \((Σ|F_o|−|F_e|)/|F_o|\) of 0.451 and a weighted \(R_1\) index \((Σw(F_o−|F_e|)^2)/ΣwF_o^2\) 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 Cd\(^{2+}\) ions lowered the error indices to \(R_1=0.117\) and \(R_2=0.112\).

The occupancy number of Cd\(^{2+}\) 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 Cd\(^{2+}\) 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 Cd4-A at 750°C treated with 0.1 torr
Cs vapor at 250°C for 12 hrs. Full-matrix least-squares refinement was initiated using the atomic parameters of the framework atoms [\(\text{Si, Al, O(1), O(2), and O(3)}\)] of dehydrated \(\text{Ag}_{2}\text{Cs}_{4}\text{Al}_{2}\text{A}^{12}\). 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) of peak height 37.7(5) \(\text{eA}^{-3}\), (0.275, 0.275, 0.275) of peak height 49.8(3) \(\text{eA}^{-3}\), and (0.107, 0.107, 0.107) of peak height 18.3(3) \(\text{eA}^{-3}\). Anisotropic refinement of the framework atoms and the Cs\(^+\) ions at Cs(1), Cs(2), and Cs(3) converged to \(R_1=0.092\) 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) \(\text{eA}^{-3}\) at (0.255, 0.255, 0.5). This peak refined with an unusually large thermal parameter. Therefore, the isotropic thermal parameter of Cs(4) was fixed at the more reasonable value given in Table 1. Allowing all occupancies of Cs(i), \(i=1\) to 4 to vary revealed 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) cannot 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) \(\text{Å}\)). 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) \(\text{eA}^{-3}\).

For all structures, the full-matrix least-squares program used minimized \(\Sigma w(F_\text{calc}-F_\text{obs})^2\); the weight(es) of an observation was the reciprocal square
of \( \sigma_p^2 \), its standard deviation. Atomic scattering factors for \( \text{Cd}^{2+}, \text{Cs}^+, \text{O}^-, \) and (Si, Al) were used. The function describing (Si, Al) is the mean of the Si\( ^{2-} \), Si\( ^{4+} \), Al\( ^{3+} \), and Al\( ^{3+} \) functions. All scattering factors were modified to account for the anomalous dispersion correction. 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 Cd\( _2 \)-A, all six Cd\( ^{2+} \) ions occupy threefold-axis positions near 6-ring, recessed 0.460(3) \( \text{Å} \) into the sodalite cavity from the (111) plane at O(3) (see Fig. 1). Each of these Cd\( ^{2+} \) ions is coordinated to three O(3) framework oxygens at 2.18(2) \( \text{Å} \). For comparison, the sum of the conventional ionic radii of Cd\( ^{2+} \) and O\( ^{-} \) is 2.29 \( \text{Å} \). The angle of O(3)-Cd-O(3) has 115.7(4)\(^\circ \), close to the trigonal planar angle (see Table 2 and Fig. 1).

Upon treating dehydrated Cd\( _2 \)-A with 0.1 torr of Cs vapor at 250°C, all six Cd\( ^{2+} \) ions in Cd\( _2 \)-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) \( \text{Å} \) into the large cavity from the (111) plane at O(3) and coordinates to three O(3) oxygens of the 6-ring at 3.13(3) \( \text{Å} \). 2.0 Cs\( ^+ \) ions at Cs(3) are also on threefold axes and associate with 6-rings, but they are recessed 1.890(12) \( \text{Å} \) into the sodalite cavity from the (111) plane.

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**Table 2. Selected Interatomic Distances (\( \text{Å} \)) and Angles (deg)**

<table>
<thead>
<tr>
<th></th>
<th>Crystal 1</th>
<th>Crystal 2</th>
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</thead>
<tbody>
<tr>
<td>( \text{Si, Al-O(1)} )</td>
<td>1.61(1)</td>
<td>1.61(4)</td>
</tr>
<tr>
<td>( \text{Si, Al-O(2)} )</td>
<td>1.64(2)</td>
<td>1.71(4)</td>
</tr>
<tr>
<td>( \text{Si, Al-O(3)} )</td>
<td>1.71(1)</td>
<td>1.62(9)</td>
</tr>
<tr>
<td>( \text{Cd-O(3)} )</td>
<td>2.18(2)</td>
<td></td>
</tr>
<tr>
<td>( \text{Cs(1)-O(1)} )</td>
<td></td>
<td>3.38(3)</td>
</tr>
<tr>
<td>( \text{Cs(1)-O(2)} )</td>
<td></td>
<td>3.51(3)</td>
</tr>
<tr>
<td>( \text{Cs(2)-O(3)} )</td>
<td></td>
<td>3.13(3)</td>
</tr>
<tr>
<td>( \text{Cs(3)-O(3)} )</td>
<td></td>
<td>3.10(7)</td>
</tr>
<tr>
<td>( \text{Cs(4)-O(1)} )</td>
<td></td>
<td>3.05(2)</td>
</tr>
<tr>
<td>( \text{Cs(4)-O(3)} )</td>
<td></td>
<td>3.01(1)</td>
</tr>
<tr>
<td>( \text{Cs(1)-Cs(2)} )</td>
<td>5.14(1)</td>
<td></td>
</tr>
<tr>
<td>( \text{Cs(1)-Cs(4)} )</td>
<td>4.30(10)</td>
<td></td>
</tr>
<tr>
<td>( \text{Cs(2)-Cs(2)} )</td>
<td>5.41(2)</td>
<td></td>
</tr>
<tr>
<td>( \text{Cs(2)-Cs(3)} )</td>
<td>3.67(1)</td>
<td></td>
</tr>
<tr>
<td>( \text{Cs(2)-Cs(4)} )</td>
<td>2.76(2)</td>
<td></td>
</tr>
<tr>
<td>( \text{Cs(3)-Cs(3)} )</td>
<td>4.57(2)</td>
<td></td>
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</tbody>
</table>

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

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**Fig. 1.** A stereoview of large cavity of vacuum dehydrated Cd\( _2 \)-A at 750°C. Six Cd\( ^{2+} \) ions at Cd is shown. Ellipsoids of 20% probability are used.

**Fig. 2.** A stereoview of a large cavity in Cs\( _2 \)-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.
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_{127}-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 $-12^{24}$. Therefore about 1/2 Cs species is too many in Cs_{127}-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_{127}-A and Cs_{87}-A. In Cs_{127}-A, two adjacent 6-rings in each large cavity are occupied by sodalite-unit Cs$^+$ ions, allowing one Cs$^+$ ion to lie 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_{87}-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_{6})$^{1+}$ cluster). All unit cells have 3 Cs$^+$ ions at Cs(1).

Cs_{87}-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 is 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 delocalization (Cs(2)-Cs(3) = 3.67(1) Å. Thus, these Cs species are associated with each other to form linear (Cs_{6})$^{3+}$ cations. (Cs_{6})$^{3+}$ clusters lie on threefold axes and extend through the center of sodalite unit. Linear (Cs_{6})$^{3+}$ clusters are also found in the structure of dehydrated Na_{127}-A reacting with cesium vapor. These (Cs_{6})$^{3+}$ clusters form a linear array with interspaces 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_{6})$^{3+}$ 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 $\rightarrow$ 4) is allowed near the middle of the visible range at about 5115 Å, which could account for the black color of the (Cs_{6})$^{3+}$ 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)

<table>
<thead>
<tr>
<th></th>
<th>Crystal 1</th>
<th>Crystal 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(2)</td>
<td>0.294(12)</td>
<td>0.135(27)</td>
</tr>
<tr>
<td>Cd(2)</td>
<td>-0.460(3)</td>
<td></td>
</tr>
<tr>
<td>Cs(2)</td>
<td>1.858(5)</td>
<td>1.809(12)</td>
</tr>
<tr>
<td>Cs(3)</td>
<td>-1.00(1)</td>
<td></td>
</tr>
</tbody>
</table>

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

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 cell. These water molecules react with Cs vapor and Cd²⁺ ions at 25°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=2x10⁻⁴ 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.

ACKNOWLEDGEMENT

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인용문헌

18. Reference 17, pp. 149–150.