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Near Zero Coordinate Ca²⁺ and Sr²⁺ in Zeolite A. Crystal Structures of Dehydrated Ca₆-A and Sr₆-A

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Abstract: The crystal structures of vacuum-dehydrated fully Ca^{2+}-exchanged zeolite A ($a = 12.278$ (2) Å) and vacuum-dehydrated fully Sr^{2+}-exchanged zeolite A ($a = 12.316$ (2) Å) have been determined by single-crystal x-ray diffraction methods in the cubic space group $Pm3m$. The structures were refined to final R (weighted) indices of 0.066 and 0.096, respectively. In each structure, five divalent cations are located on threefold axes near the centers of 6-oxygen rings. In Ca_6-A, the five Ca^{2+} ions are located at three unique equipoints: three equivalent ions are recessed 0.51 Å into the large cavity; one is nearly in the plane of a 6-oxygen ring; the fifth is 0.63 Å into the sodalite unit. The five threefold-axis Sr^{2+} ions occupy two equipoints: three equivalent ions are recessed 0.28 Å into the large cavity, and two are 0.78 Å into the sodalite unit, on opposite sides of the origin. The sixth Ca^{2+} ion is located at an unusual position in the plane of an 8-oxygen ring, and the sixth Sr^{2+} ion occupies a similar site near this plane. This Ca^{2+} ion is 3.08 (4) Å from its nearest neighbor, a single oxide ion of the aluminosilicate framework—this exceeds the sum of the respective ionic radii by 0.77 Å. (Two other oxide ions are 3.13 (6) Å from this Ca^{2+} ion.) The corresponding Sr^{2+} ion is 2.96 (12) Å from its nearest neighbor, a framework oxide ion—this distance is 0.52 Å longer than the sum of the corresponding ionic radii. (Two other oxide ions are 2.98 (13) Å from this Sr^{2+} ion.) These discrepancies are especially significant because the conventional ionic radii used are appropriate for larger coordination numbers and should be too long to describe the low-coordinate situation of the 8-ring cation. Presumably, one ion is located in an 8-ring in each structure because this allows a more satisfactory distribution of positive charge than would be possible if all six cations per unit cell occupied threefold-axis sites.

Introduction

The crystal structure of dehydrated Ca_4Na_4-A,[1,2] determined using x-ray powder diffraction data, shows that the eight exchangeable cations per unit cell occupy the eight 6-ring[3] sites. These sites are apparently preferred by Ca^{2+} and Na^+, and it was anticipated that all exchangeable cations in dehydrated further Ca^{2+}-exchanged zeolite A, Ca_xNa_{12-2x}-A, $4 < x \leq 6$, would locate at 6-ring sites. Subsequent work with Mn(II),[4,5] CO(II),[5,6] and Zn(II)[5,7] incompletely exchanged into zeolite A also shows all divalent cations to be located at 6-ring sites upon vacuum dehydration.

The crystal structure of dehydrated Eu_xNa_{12-2x}-A,[8] $5.5 \leq x \leq 6.0$, possibly a fully Eu(II)-exchanged material, shows that, although most Eu(II) ions are located at 6-ring sites, both 8-ring and 4-ring sites are also occupied, even though additional 6-ring sites are available. Most interesting is the presence of one Eu(II) ion per unit cell at the very center of an 8-oxygen ring, 3.4 Å from the four nearest oxide ions of the aluminosilicate framework of the zeolite—*this distance is approximately 1.0 Å more than the sum of the corresponding ionic radii.*[9] This result suggested immediately that similar unusual coordination geometries might occur commonly in dehydrated fully divalent-cation-exchanged zeolite A.

Large monovalent cations that are zero coordinate[10-13] (K^+ and Rb^+) or near zero coordinate[14] (Tl^+) have been found in various exchanged forms of zeolite A. The principles involved have been discussed.[11-14] Qualitatively different principles would describe the zero coordination of divalent cations. *A far more diverse and interesting chemistry can be envisioned for*

zero and near zero coordinate divalent cations, which could include many transition metal ions, than might be expected for the large alkali-metal monovalent cations.

In order to explain the sorption of gases by Ca^{2+}-exchanged zeolite A as a function of its calcium content, Takaishi and co-workers[15] concluded, using percolation theory, that one Ca^{2+} ion per unit cell in dehydrated Ca_6-A is located at an 8-ring site. They were also able to learn that this 8-ring Ca^{2+} ion is relatively easily displaced from its window-blocking position, indicating it to be weakly held and to have a high thermal parameter. This unexpected finding is very much in accord with the structural results on Eu(II)-exchanged zeolite A.[8]

The locations of the Ca^{2+} ions in hydrated Ca_6-A are surprisingly irregular.[16] Three Ca^{2+} ions are recessed far into the sodalite cavity, and three lie relatively far into the large cavity, positions quite different from those found for Ca^{2+} ions in hydrated Ca_4Na_4-A.[17] By showing that six divalent cations occupy sites dissimilar to those in a four-divalent-cation exchanged hydrated structure, this work[11] encouraged hopes that dehydrated structures as unusual as that of Eu_xNa_{12-2x}-A,[8] $5.5 \leq x \leq 6.0$, would be found upon full exchange with other divalent cations.

To establish the existence of zero or near zero coordinate divalent cations in addition to Eu(II) in zeolite A, and to better define the principles involved, work on the structures of dehydrated Ca_6-A and Sr_6-A was initiated. Ion exchange using these alkali-earth cations was expected to be facile and complete.[18] The ionic radii[8] of Ca^{2+} (0.99 Å) and Sr^{2+} (1.12 Å) are similar to that of Eu(II) (1.09 Å). Finally, the preparation

Table I. Positional, Thermal, and Occupancy Parameters

Atom	Wyckoff position	x	y	z	β_{11} or B_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy factor
				a. Ca_6-A, Dehydrated							
(Si,Al)	24(k)	0	1828 (3)	3715 (2)	40 (3)	22 (2)	17 (2)	0	0	4 (4)	1[c]
O(1)	12(h)	0	2190 (8)	1/2	75 (11)	54 (9)	25 (8)	0	0	0	1
O(2)	12(i)	0	2882 (6)	2882 (6)	148 (15)	35 (5)	35 (5)	0	0	42 (16)	1
O(3)	24(m)	1116 (4)	1116 (4)	3383 (5)	43 (4)	43 (4)	53 (6)	22 (10)	3 (7)	3 (7)	1
Ca(1)	8(g)	2113 (10)	2113 (10)	2113 (10)	67 (9)	67 (9)	67 (9)	68 (20)	68 (20)	68 (20)	3/8
Ca(2)	8(g)	1908 (21)	1908 (21)	1908 (21)	0.3 (6)[d]						1/8
Ca(3)	8(g)	1578 (15)	1578 (15)	1578 (15)	1.4 (6)[d]						1/8
Ca(4)	12(i)	0	4683 (35)	4683 (35)	1376 (329)	91 (52)	91 (52)	0	0	35 (97)	1/12
				b. Sr_6-A, Dehydrated							
(Si,Al)	24(k)	0	1832 (4)	3733 (3)	25 (4)	20 (3)	11 (3)	0	0	1 (6)	1[c]
O(1)	12(h)	0	2242 (13)	1/2	70 (17)	21 (17)	58 (17)	0	0	0	1
O(2)	12(i)	0	2845 (9)	2845 (9)	49 (15)	22 (7)	22 (7)	0	0	29 (21)	1
O(3)	24(m)	1146 (5)	1146 (5)	3459 (9)	24 (5)	24 (5)	48 (9)	26 (15)	20 (11)	20 (11)	1
Sr(1)	8(g)	2050 (6)	2050 (6)	2050 (6)	63 (5)	63 (5)	63 (5)	97 (13)	97 (13)	97 (13)	3/8
Sr(2)	8(g)	1550 (10)	1550 (10)	1550 (10)	73 (8)	73 (8)	73 (8)	56 (19)	56 (19)	56 (19)	2/8
Sr(3)	24(m)	723 (300)	4476 (37)	4476 (37)	1169 (654)	77 (33)	77 (33)	−148 (241)	−148 (241)	50 (92)	1/24

[a] Positional and anisotropic thermal parameters are given $\times 10^4$. Numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding parameter. See Figures 2–5 for the identities of the atoms. The anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] Root mean square displacements can be calculated from β_{ii} values using the formula $\mu_i = 0.225a(\beta_{ii})^{1/2}$. [c] Occupancy for (Si) = 1/2; occupancy for (Al) = 1/2. [d] Isotropic thermal parameter in units of $Å^2$.

procedures would be far easier and less open to question, because these cations, unlike Eu(II), would not be sensitive to oxidation by trace amounts of O_2.

Experimental Section

Single crystals of the synthetic molecular sieve zeolite 4A, Na_{12}-A, were prepared by Charnell's method,[19] modified to include a second crystallization using seed crystals from the first synthesis. A single crystal 0.08 mm on an edge was lodged in a fine glass capillary for each exchange. Ion exchange was performed by flow methods—a continuous stream of fresh solution ($Ca(OH)_2$ or $Sr(OH)_2$) flowed past the crystal at a velocity of approximately 1.0 cm/s for 5 days at 25 (1) °C. Saturated solutions of $Ca(OH)_2$ (Mallinckrodt, analytical reagent) and $Sr(OH)_2$ (Ventron/Alfa, 99.99% purity) were used; their concentrations were 0.025 and 0.034 M, respectively. This corresponds to a complete refreshment of the exchange solution about 100 times per second; since the exchange of Ca^{2+} and Sr^{2+} for Na^+ has been shown to be complete after much milder treatment,[18] complete exchange was assured in this work. After the solutions were drained, no noticeable droplet of solution remained near either crystal, and a rinse step, which might have caused some H^+ exchange, was not performed. After dehydration at 350 °C and 5×10^{-6} Torr for 48 h, the crystals were allowed to cool to room temperature, and were sealed in their still-evacuated capillaries by torch. The microscopic appearances of the two crystals were unaltered by the exchange and dehydration procedures, suggesting that no crystal damage had occurred. The dehydrated Ca_6-A crystal was colorless, and that of Sr_6-A was faintly yellow.

An attempt was made to extend this alkaline-earth series to include Ba_6-A, even though dehydration of zeolite A which had been exchanged with aqueous 0.1 M $BaCl_2$ had been reported to result in the destruction of the structure.[20,21] Ion exchange using aqueous 0.2 M $Ba(OH)_2$ was conducted with the hope that partial proton exchange, which might have occurred previously and could have been responsible for the destruction of the crystal upon dehydration, would be prevented. Exchange by the flow method (described above) proceeded for 5 days, and was followed by evacuation at 5×10^{-6} Torr and 350 °C for 48 h. The resulting crystal was white and opaque, and had developed a weathered appearance; x-ray examination indicated that the zeolite A structure had been destroyed.

Analyses for calcium and strontium were not performed; the unit cell compositions of $Ca_6Si_{12}Al_{12}O_{48}$ and $Sr_6Si_{12}Al_{12}O_{48}$ were confirmed by refinement of the diffraction data.

X-Ray Data Collection. The space group $Pm3m$ (no systematic absences) was used throughout this work for reasons discussed previously.[22,23] Preliminary crystallographic experiments and subsequent data collection were performed with an automated, four-circle Syntex $P\bar{1}$ diffractometer, equipped with a graphite monochromator and a pulse-height analyzer. Molybdenum radiation was used for all experiments ($K\alpha_1$, $\lambda = 0.709\ 30$ Å; $K\alpha_2$, $\lambda = 0.713\ 59$ Å). The cubic unit cell constants, as determined by least-squares refinement of 15 intense reflections ($20° < 2\theta < 24°$ in each case), are 12.278 (2) Å and 12.316 (2) Å for Ca_6-A and Sr_6-A, respectively.

Reflections from two intensity-equivalent regions of reciprocal space (hkl, $h \leq k \leq l$, and lhk, $l \leq h \leq k$) were examined by θ–2θ scans at a constant rate of 1.0 deg min^{-1} from 0.8° (in 2θ) below the calculated $K\alpha_1$ peak to 0.8° above the $K\alpha_2$ maximum. Background intensity was counted at each end of a scan range for a time equal to half the scan time. The intensities of three reflections, (0,5,5), (5,0,5), and (5,5,0), were recorded after every 100 reflections to monitor crystal and instrument stability. Only small, random fluctuations of these check reflections were noted during the course of data collection.

The intensities of all lattice points with $2\theta < 70°$ were recorded. Although few reflections were significantly greater than background for high 2θ values, this limit was selected to give a more complete data set.

The raw data for 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 averaged reflection by the computer program COMPARE.[24] Other details regarding data reduction have been discussed previously.[14] No absorption correction was applied. Of the 884 and 891 unique pairs of reflections examined for Ca_6-A and Sr_6-A, respectively, only the 303 and 307 whose net counts exceeded three times their corresponding esd's after merging were used in structure solution and refinement.

Structure Determination. Ca_6-A. Full-matrix least-squares refinement of the structure was initiated using the atomic parameters of Ca_4Na_4-A[1] for the atoms of the aluminosilicate framework ((Si,Al), O(1), O(2), and O(3)) and for one threefold-axis Ca^{2+} position near the 6-ring planes. Anisotropic temperature factors were employed in the refinement of all ions, except for the Ca^{2+} position; it was refined isotropically with the simultaneous refinement of its occupancy parameter. This model quickly converged to $R_1 = (\Sigma|F_o - |F_c||/\Sigma F_o) = 0.122$ and $R_2 = (\Sigma w(F_o - |F_c|)^2/\Sigma wF_o^2)^{1/2} = 0.123$. The occupancy of the Ca^{2+} position was approximately five ions per unit cell with a somewhat large isotropic thermal parameter. A subsequent difference Fourier synthesis indicated that the input Ca^{2+} position could better be described by two separate positions, Ca(1) and Ca(2) (see Table Ia), with occupancies of at least three ions and at least one ion per unit cell, respectively. Another peak 2.8 e $Å^{-3}$ in height on a threefold axis at (0.15, 0.15, 0.15) indicated the presence
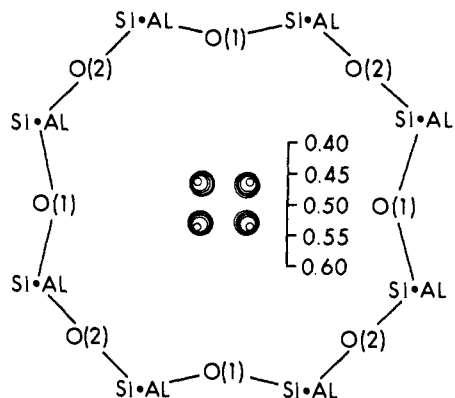
Figure 1. The electron density function for Ca₆-A in the plane of the 8-oxygen ring. Contours are drawn at intervals of 0.5 e Å⁻³; the electron density maximum is 2.5(1) e Å⁻³. These peaks are especially long along the direction of view, as can be easily seen for the Ca(4) ion at the right side of Figure 2.
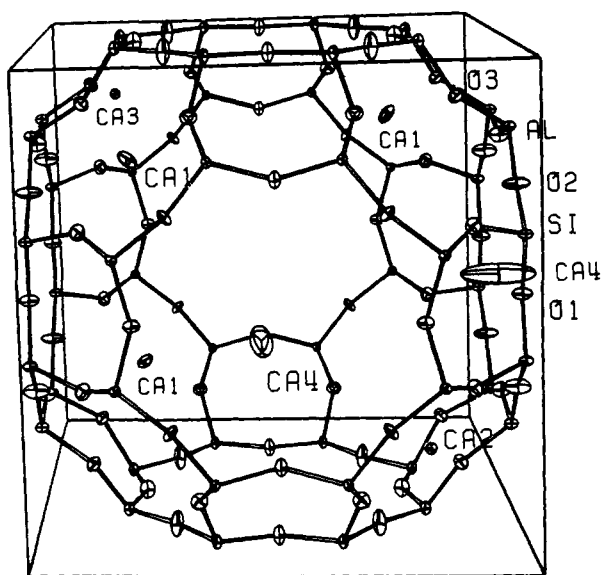

Figure 2. A view of the large cavity of Ca₆-A. Ellipsoids of 20% probability are shown. The thermal parameter on Ca(2) was increased by 1.5σ for the purposes of the drawing. The Ca²⁺ coordinates are given in Table IV.

of a third Ca²⁺ position in the sodalite unit, at Ca(3). Also, in the plane of the 8-ring, a peak 1.7 e Å⁻³ in height at (0.0, 0.46, 0.46) clearly indicated the presence of a Ca²⁺ ion at Ca(4). This peak density is suitable for one Ca²⁺ ion distributed within a 12-fold equipoint. Figure 1 shows four peaks which together represent the electron density due to one-third of one Ca²⁺ ion at Ca(4) in a particular 8-ring plane. (See also Table Ia and Figures 2 and 3.)

Simultaneous occupancy, positional, and thermal parameter refinement of the ions located on the threefold axes was not successful, presumably because of the close proximity of the Ca²⁺ ions at Ca(1), Ca(2), and Ca(3). However, a more piecemeal refinement of the threefold-axis Ca²⁺ ions led to the lowest R values and to a relatively featureless final difference Fourier synthesis. That is, with the occupancies of Ca(1), Ca(2), and Ca(3) fixed, their positional and thermal parameters were refined to convergence. Then with positional parameters fixed, their occupancies and thermal parameters were allowed to vary. Finally, the occupancies of Ca(1), Ca(2), and Ca(3) were fixed at the values shown in Table Ia as all other parameters were refined to convergence.

The addition of Ca(4), the 8-ring Ca²⁺ ion, lowered R_2 by 0.023. An attempt to refine Ca(4) with a nonzero x coordinate was successful, but the esd's of the parameters were so large and the shifts in least-squares so erratic that this model, with its two extra parameters, x and β_{12}, was not accepted. Specifically, the β_{11} parameter for this model, 0.12 (7), is very uncertain and nearly as large as the value in Table Ia, 0.14 (3); the x coordinate is 0.04 (3).

Occupancy refinement with other parameters fixed indicated 1.4 (2) ions at Ca(4); this value was rounded to the nearest integer, 1, by the assumption of stoichiometry and the requirement of electrical neutrality, that the total number of Ca²⁺ ions per unit cell not exceed six. Least-squares refinement using anisotropic thermal parameters was successful for the framework atoms, Ca(1), and Ca(4); Ca(2) and Ca(3) were refined isotropically. This model (Table Ia) converged to the final error indices, $R_1 = 0.084$ and $R_2 = 0.066$.

The goodness of fit, $(\Sigma w(F_o - |F_c|)^2/(m - s))^{1/2}$, is 3.08; m (303) is the number of observations, and s (32) is the number of variables in least squares. All shifts in the final cycle of refinement were less than 3% of their esd's, except for the anisotropic β's of Ca(4), whose shifts were about 25% of their esd's.

On the final difference Fourier function, whose estimated standard deviation is 0.1 e Å⁻³, the largest peak was 1.3 e Å⁻³ in height and was on a threefold axis very near the Ca(3) position.

Sr₆-A. Initial full-matrix least-squares refinement began with the framework atomic parameters of Ca₆-A and included, as a guess, three Sr²⁺ ions at Sr(1) and two Sr²⁺ ions at Sr(2) (see Table Ib). Anisotropic thermal parameters were used in the refinement of all positions except Sr(1) and Sr(2), which were refined isotropically; this procedure converged to the error indices $R_1 = 0.148$ and $R_2 = 0.135$, respectively. Simultaneous occupancy, positional, and anisotropic thermal parameter refinement of Sr(1) and Sr(2) indicated 3.3 ions at Sr(1) and 2.3 ions at Sr(2). By the assumption of stoichiometry, these values were rounded to the integers 3 and 2, respectively, and were held fixed thereafter. A subsequent difference Fourier synthesis revealed the position of the remaining Sr²⁺ ion, Sr(3), near the plane of the 8-ring at (0.075, 0.45, 0.45) with a peak height of 1.4 e Å⁻³, a suitable value for one Sr²⁺ ion distributed within a 24-fold equipoint. This peak was stable in least-squares refinement as one Sr²⁺ ion. Occupancy refinement converged to 1.3 ions at Sr(3) and was rounded to the integer 1, to give a total of six Sr²⁺ ions per unit cell. Adding the ion at Sr(3) lowered R_1 by 0.008 and R_2 by 0.027, significant amounts. Anisotropic refinement of the six-Sr²⁺ model converged with the final error indices, $R_1 = 0.111$ and $R_2 = 0.096$. The final structure is presented in Table Ib and Figures 4 and 5.

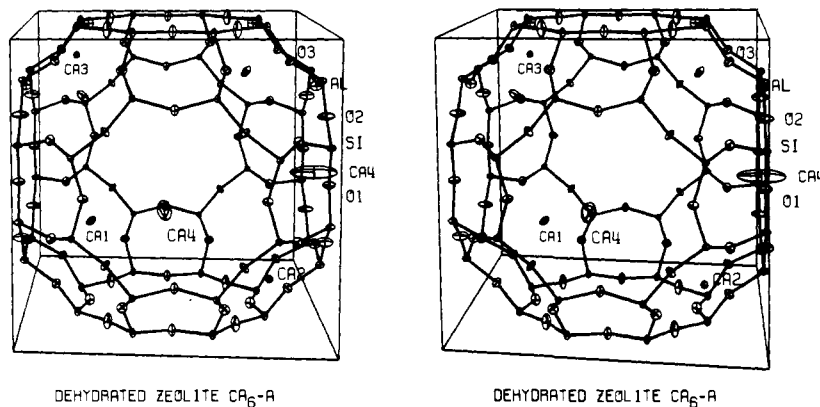The goodness of fit is 4.54; the number of observations is 307; 33

DEHYDRATED ZEOLITE CA₆-A

DEHYDRATED ZEOLITE CA₆-A

Figure 3. A stereoview of Ca₆-A. Other comments in the caption to Figure 2 apply here as well.

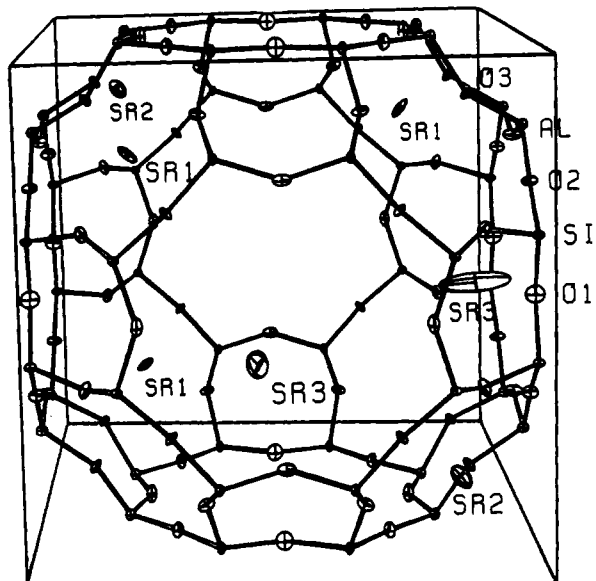**Figure 4.** A view of the large cavity of Sr_6-A. The Sr(3) ion in the front 8-ring lies in an adjacent unit cell. Ellipsoids of 20% probability are shown. The Sr^{2+} coordinates are given in Table IV.

Table II. Selected Interatomic Distances (Å) and Angles (deg)[a]

a. Ca_6-A		b. Sr_6-A	
(Si,Al)–O(1)	1.640 (4)	(Si,Al)–O(1)	1.640 (6)
(Si,Al)–O(2)	1.649 (3)	(Si,Al)–O(2)	1.659 (4)
(Si,Al)–O(3)	1.676 (3)	(Si,Al)–O(3)	1.679 (4)
Ca(1)–O(3)	2.328 (8)	Sr(1)–O(3)	2.343 (9)
Ca(2)–O(3)	2.272 (7)	Sr(2)–O(3)	2.454 (12)
Ca(3)–O(3)	2.356 (11)	Sr(3)–O(1)	2.96 (12)
Ca(4)–O(1)	3.08 (4)	Sr(3)–O(2)	2.98 (13)
Ca(4)–O(2)	3.13 (6)		
		O(1)–(Si,Al)–O(2)	113.3 (8)
O(1)–(Si,Al)–O(2)	112.5 (6)	O(1)–(Si,Al)–O(3)	110.2 (5)
O(1)–(Si,Al)–O(3)	112.0 (3)	O(2)–(Si,Al)–O(3)	104.2 (5)
O(2)–(Si,Al)–O(3)	104.9 (4)	O(3)–(Si,Al)–O(3)	114.4 (5)
O(3)–(Si,Al)–O(3)	109.9 (5)		
		(Si,Al)–O(1)–(Si,Al)	144 (1)
(Si,Al)–O(1)–(Si,Al)	148.4 (8)	(Si,Al)–O(2)–(Si,Al)	172 (1)
(Si,Al)–O(2)–(Si,Al)	166.7 (7)	(Si,Al)–O(3)–(Si,Al)	143.6 (8)
(Si,Al)–O(3)–(Si,Al)	142.5 (5)		
		O(3)–Sr(1)–O(3)	118.5 (7)
O(3)–Ca(1)–O(3)	115.3 (9)	O(3)–Sr(2)–O(3)	110.3 (3)
O(3)–Ca(2)–O(3)	120 (2)	O(1)–Sr(3)–O(1)	108 (8)
O(3)–Ca(3)–O(3)	113.2 (5)	O(1)–Sr(3)–O(2)	55 (4)
O(1)–Ca(4)–O(1)	104 (2)		
O(1)–Ca(4)–O(2)	52 (1)		

[a] Numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding value.

Table III. Deviations of Atoms (Å) from the (111) Plane at O(3)[a]

	Ca_6-A		Sr_6-A
Ca(1)	0.51	Sr(1)	0.28
Ca(2)	0.06	Sr(2)	−0.78
Ca(3)	−0.63	O(2)	−0.04
O(2)	0.11		

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

variables were refined. All shifts in the final cycle of refinement were less than 1.5% of their corresponding esd's.

On the final difference Fourier function, whose estimated standard deviation is 0.14 e Å^{-3} at a general position, the largest peak was 2.2 e Å^{-3} in height and was on a threefold axis at $x = y = z = 0.29$. This position was unstable in least squares and developed a very large thermal parameter even though the relatively small O^- scattering factor was used. The R values did not decrease, and the occupancy parameter refined to zero. Beyond that, this peak is only 1.7 Å from Sr(1), too close to be a coordinated water oxygen.

The final structural parameters for Ca_6-A and Sr_6-A are presented in Tables Ia and Ib, respectively. Interatomic distances and angles are given in Table II. Ca^{2+} and Sr^{2+} fractional coordinates as plotted in Figures 2–5 are shown in Table IV. A listing of observed and calculated structure factors is available; see the paragraph at the end of the paper regarding supplementary material.

Likely arrangements of the exchangeable cations in particular unit cells of Ca_6-A and Sr_6-A are shown in Figures 2 and 4, respectively. These have not been established crystallographically and may not exist in every unit cell—they are only most likely arrangements, strictly consistent with the disordered structural models which emerged from the crystallographic calculations. Their symmetry is 1. Stereoviews are shown in Figures 3 and 5.

The full-matrix least-squares program used[24] minimized $\Sigma w(\Delta|F|)^2$; the weight (w) of an observation was the reciprocal square of σ, its standard deviation. Atomic scattering factors[25] for Ca^{2+}, Sr^{2+}, O^-, and $(Si,Al)^{1.75+}$ were used. 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 the real component $(\Delta f')$ of the anomalous dispersion correction.[26]

Discussion

Dehydrated Ca_6-A. In the structure of dehydrated Ca_6-A (Tables Ia, IIa, III, and IV and Figures 1, 2, and 3), five Ca^{2+} ions are distributed over three nonequivalent threefold-axis equipoints. Three ions at Ca(1) extend 0.51 Å into the large cavity from the O(3) planes of the oxygen 6-rings; one at Ca(2) lies nearly in the O(3) plane; and the fifth ion, at Ca(3), is in the sodalite unit, 0.63 Å from the [111] plane at O(3). The ions at Ca(1), Ca(2), and Ca(3) are trigonally coordinated to their respective sets of three O(3) framework oxide ions at 2.325,

DEHYDRATED ZEOLITE SR_6-A
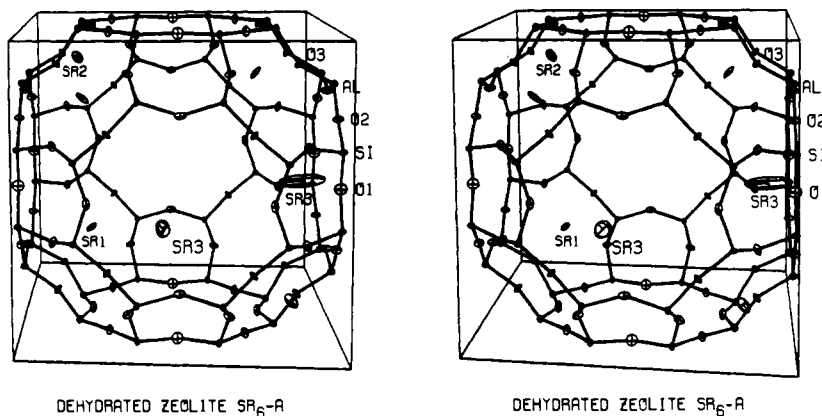

DEHYDRATED ZEOLITE SR_6-A

Figure 5. A stereoview of Sr_6-A. Other comments in the caption to Figure 4 apply here as well.

Table IV. Ca^{2+} and Sr^{2+} Fractional Coordinates Plotted[a] in Figures 2–5

Ca₆-A				Sr₆-A			
Ca(1)	0.7887	0.2113	0.2113	Sr(1)	0.7950	0.2050	0.2050
Ca(1)	0.2113	0.2113	0.7887	Sr(1)	0.2050	0.2050	0.7950
Ca(1)	0.2113	0.7887	0.2113	Sr(1)	0.2050	0.7950	0.2050
Ca(2)[b]	0.8092	0.8092	0.8092	Sr(2)[b]	0.1550	0.1550	0.1550
Ca(3)[b]	0.1578	0.1578	0.1578	Sr(2)[b]	0.8450	0.8450	0.8450
Ca(4)	1.00	0.5317	0.4683	Sr(3)	0.9277	0.4476	0.5524
Ca(4)	0.4683	0.5317	1.00	Sr(3)[c]	0.4476	0.5524	1.0723

[a] The coordinate system used is $+x$ to the right, $+y$ downward in the plane of the page, and $+z$ up from the page. [b] These ions lie on the same threefold axis. [c] This position is in an adjacent unit cell.

2.272, and 2.356 Å. The principal cation position, Ca(1), is nearly the same as the calcium position in dehydrated Ca_4Na_4-A.[1]

A plausible and unique relative arrangement of these five threefold-axis cations, one in which one threefold axis is preserved, is presented in Figures 2 and 3. The Ca^{2+} ions have been placed within their partially occupied equipoints so as to minimize their electrostatic repulsions (by maximizing the shorter of their intercationic approaches) and to maximize the distribution of positive charge (to balance most evenly the anionic charge of the zeolite framework). To minimize electrostatic repulsions, it is necessary that the ions at Ca(2) and Ca(3) be on the same threefold axis, associated with two opposite 6-rings of the small (or large) cavity, on opposite sides of the origin.

The remaining ion at Ca(4) is located in the plane of the 8-ring, off its center, and on a diagonal mirror plane. It approaches three framework oxide ions at approximately equal distances, 3.08 Å to two ions at O(1) and 3.13 Å to one at O(2). The average of these approaches (3.11 Å) is 0.80 Å greater than the sum of the corresponding ionic radii,[9] 2.31 Å, which is equal to the most precise corresponding approach in this structure, the Ca(1)–O(3) coordination distance. The relatively large thermal parameters of the ion at Ca(4) are entirely consistent with its long and presumably weak interaction with the zeolite framework. To maximize the shorter intercationic distances and the distribution of positive charge, the ions (one per unit cell) at Ca(4) have been placed in adjacent 8-rings in Figures 2 and 3.

The presence of an ion at Ca(4) is in complete accord with Takaishi's result, which was reached by the percolation-theory analysis of sorption experiments,[15] that one Ca^{2+} ion is located in an 8-oxygen ring, and that it is loosely held.

Dehydrated Sr₆-A. The crystal structure of Sr₆-A (Tables Ib, IIb, III, and IV and Figures 4 and 5) is very similar to that of Ca₆-A. Five Sr^{2+} ions are distributed over two nonequivalent threefold-axis equipoints. Three ions at Sr(1) extend 0.28 Å into the large cavity from the [111] plane at O(3), and two at Sr(2) lie in the sodalite unit 0.78 Å from the O(3) plane.

As in Ca₆-A, a unique relative distribution of these five cations has emerged which minimizes intercationic repulsions and preserves one threefold axis (see Figures 4 and 5). The two cations at Sr(2) lie in the sodalite unit of this unique threefold axis, on opposite sides of the origin. The three ions at Sr(1) in the large cavity occupy three of the remaining six 6-rings, one of the two sets of three 6-rings which are symmetrically placed about the unique threefold axis.

The ions at Sr(1) and Sr(2) are each trigonally coordinated to their respective sets of three O(3) oxide ions at 2.34 and 2.45 Å.

As in dehydrated Ca₆-A, the sixth Sr^{2+} ion in Sr₆-A is associated with an 8-ring. Its closest approaches to the framework, to two oxide ions at O(1) and one at O(2) in an 8-ring, are 2.96 and 2.98 Å, respectively, approximately 0.52 Å greater than the sum of the corresponding ionic radii,[9] 2.44 Å. The very

elongated thermal ellipsoid of this Sr^{2+} ion is consistent with the long and presumably weak approaches that it makes to these framework oxygens. Unlike the cation at Ca(4) in Ca₆-A, Sr(3) does not lie in the plane of the 8-ring; it is approximately 0.9 Å from it. The cations at Sr(3) (one per unit cell) have been placed in adjacent 8-rings (see Figures 4 and 5) for the same reasons as in Ca₆-A.

The Eight-Ring Cations. The crystal structures of Ca₆-A and Sr₆-A demonstrate the surprising result that one divalent cation per unit cell is located at a seemingly unfavorable 8-ring site, even though three generally preferred 6-ring sites remain unoccupied and available. Presumably this situation has occurred for reasons which are largely electrostatic—to neutralize more evenly the anionic charge of the zeolite framework and to minimize intercationic repulsions. Perhaps a structure with six divalent cations on threefold axes results in an unacceptable concentration of positive charge in one area of the unit cell with a corresponding deficiency in another. Certainly a sodalite unit with five cations need have only three adjacent-6-ring cation approaches, while no fewer than six such approaches would occur if six cations were present. Approach distances to an 8-ring site are substantially longer.

The 8-ring cation in both Ca₆-A and Sr₆-A might be considered three-coordinate; it approaches one ion at O(2) and two at O(1) at nearly equal distances. The geometry, however, is far from the nearly regular trigonal coordination of the five 6-ring cations. In addition, these 8-ring cations form unusually long and weak bonds to framework oxide ions at distances significantly greater than the sum of the appropriate ionic radii.[9] These discrepancies become even more significant when it is noted that the ionic radii[9] used are appropriate for more conventional coordination numbers and geometries and should be too long, considering the very low coordination number of the 8-ring cation.[27] Thus, these cations, coordinating at distances which exceed the sum of their corresponding ionic radii by more than 0.5 Å, are termed near zero coordinate based on a distance criterion.[14]

This weak coordination may result from a tendency of the 8-ring Ca^{2+} and Sr^{2+} ions to approach three framework oxide ions at long but equal distances. Such a coordination site is apparently favored over one which forms a normal M^{2+}–O(2) bond and two somewhat longer M^{2+}–O(1) bonds. For example, consider a Ca(4) ion at the hypothetical position (0, 0.42, 0.42). Its coordination distance to a single ion at O(2) would be normal at 2.29 Å, but it would be 2.65 Å from two ions at O(1). A similar situation could be described for a Sr^{2+} ion. To achieve equal approach distances, it is suggested, the ion at Ca(4) shifts toward (0, ½, ½); the ion at Sr(3), although it shifts off the 8-ring plane, achieves the same result. It is not clear why these ions would favor longer but equal-length approaches over shorter but unequal ones.

The factors responsible for these unusual positions must involve both electrostatic and dispersive considerations, and are likely to include some of those suggested for zero and near zero coordination involving monovalent cations.[11-14]

Table V. Aluminosilicate Framework Angles (deg) in Various Fully Dehydrated Zeolite A Structures

Angle	Na$_{12}$-A[a]	K$_{12}$-A[b]	Tl$_{12}$-A[c]	Ca$_6$-A	Sr$_6$-A
O(1)-(Si,Al)-O(2)	110	108	107	113	114
O(1)-(Si,Al)-O(3)	110	111	113	112	110
O(2)-(Si,Al)-O(3)	107	108	107	105	104
O(3)-(Si,Al)-O(3)	112	110	110	110	114

[a] Reference 3a. [b] Reference 13. [c] Reference 17.

The thermal ellipsoids of the 8-ring cations in both structures are particularly elongated along directions normal, or nearly normal, to the 8-ring plane. The lengths of the closest approaches made by these cations are insensitive to displacement along these directions, so this high thermal motion is reasonable. In addition, the placement of the other Ca^{2+} ions about any particular 8-ring Ca^{2+} ion is unlikely to be symmetric, so some positional disorder is likely to be a component of this elongation. The thermal parameters of the 8-ring Sr^{2+} ions are also likely to contain some positional disorder.

Additional Discussion. Only the average O(3) position determined (because of the choice of space group and the disorder implicit in the structure) could be used to calculate the M^{2+}-O(3) distances in Ca$_6$-A and Sr$_6$-A. One would expect the conformation of a particular 6-ring to depend upon whether it contains a divalent cation or is unoccupied. The averaging of such different rings may have contributed to the relatively high final error indices in both structures.

The aluminosilicate framework angles in a number of dehydrated monovalent-cation-exchanged zeolite A structures are more regular than those of Ca$_6$-A and Sr$_6$-A (see Table V). The O-(Si,Al)-O angles in dehydrated Sr$_6$-A deviate most from tetrahedral. This may indicate a degree of structural irregularity and strain induced by the cations which could be responsible for the high final R values for dehydrated Sr$_6$-A and for the instability of dehydrated Ba$_6$-A.

It is O(3) to which the five 6-ring cations in each structure are bound. Although only five of the eight 6-rings are involved, and although only average O(3) positions have been found, the (Si,Al)-O(3) distances (also averages) are longer than (Si,Al)-O(1) and (Si,Al)-O(2) in both dehydrated Ca$_6$-A and Sr$_6$-A. The (Si,Al)-O(3) bond has been lengthened and weakened by M^{2+} coordination to O(3). This effect has been observed and discussed previously.[7,28,29]

A high catalytic activity of Ca$_6$-A for the isomerization of 1-butene has been observed and attributed to the 8-ring near zero coordinate Ca^{2+} ion.[30] Less completely exchanged samples of zeolite A, those with no 8-ring Ca^{2+} ions, were observed to be much less active. This is regarded as the first report of the direct assignment of a chemical result to a zero or near zero coordinate divalent cation. Anticipated near zero coordinate Ag$^+$ ions oxidize oxide ions to O$_2$.[31]

Supplementary Material Available: Listings of the observed and calculated structure factors for both structures (Supplementary Tables 1 and 2) (4 pages). Ordering information is given on any current masthead page.

References and Notes

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