Reaction of Dehydrated Na_{12}–A with Cesium. Synthesis and Crystal Structure of Fully Dehydrated, Fully Cs^+-Exchanged Zeolite A

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Abstract: A most ionically crowded zeolite, fully dehydrated, fully Cs^+-exchanged zeolite A, has been synthesized by the reduction of all Na^+ ions in Na_{12}–A by cesium vapor. The redox reaction goes to completion at 350 °C with 0.1 Torr of Cs^0 to give Cs_{12}–A·$^1/_2$Cs; an intermediate composition $Cs_{8.5}Na_{3.5}$–A·$^1/_2$Cs formed upon reaction at 250 °C. Two crystal structures of Cs_{12}–A·$^1/_2$Cs (a = 12.279 and 12.276 Å) and one of $Cs_{8.5}Na_{3.5}$–A·$^1/_2$Cs (a = 12.252 Å) have been determined by single-crystal X-ray diffraction methods in the cubic space group $Pm3m$ with final R (weighted) indices of 0.042, 0.042, and 0.052, respectively. Cs_{12}–A·$^1/_2$Cs may be viewed as a mixture of Cs_{12}–A and Cs_{12}–A·Cs, and $Cs_{8.5}Na_{3.5}$–A·$^1/_2$Cs, as a mixture of Cs_8Na_4–A and Cs_9Na_3–A·Cs. In each of these, three Cs^+ ions are located at the centers of 8-rings and two Cs^+ ions are found in the sodalite unit (except Cs_8Na_4–A, which has only one). In Cs_{12}–A and Cs_{12}–A·Cs, six and eight Cs^+ ions per unit cell, respectively, lie opposite 6-rings in the large cavity. In Cs_8Na_4–A and Cs_9Na_3–A·Cs, the unreacted Na^+ ions remain nearly on 6-ring planes and four Cs^+ ions are found on threefold axes deep in the large cavity, 3.00 Å from O(3) oxygens. One Cs^+ ion in Cs_{12}–A and one in Cs_8Na_4–A are found in the large cavity near a 4-ring that is adjacent to two 6-rings; these 6-rings are occupied by two sodalite-unit Cs^+ ions in Cs_{12}–A and by such a Cs^+ ion and a Na^+ ion in Cs_8Na_4–A. In each structure, 0.5 excess cesium was found per unit cell. The zeolite appears to be able to decrease the net electrostatic repulsive energy among its crowded cesium ions and to form some weak metal–metal bonds, by sorbing extra Cs atoms. Cs_{12}–A·$^1/_2$Cs and $Cs_{8.5}Na_{3.5}$–A·$^1/_2$Cs may be viewed as materials with 12.5 ions and 0.5 excess electron per unit cell. Each extra Cs atom associates with three Cs^+ ions to form a linear $(Cs_4)^{3+}$ cluster, which lies on a threefold axis and extends through the center of the sodalite unit. If the zeolite framework is silicon-rich, $(Cs_2)^+$ would be present in sodalite units of composition $Cs_{11}Si_{13}Al_{11}O_{48}$·Cs.

Fully dehydrated, fully Cs^+-exchanged zeolite A, if it could be prepared, would be a most ionically crowded zeolite. The arrangement that 12 such large ions (r_{Cs^+} = 1.67 Å)[1] would adopt in a 12.3-Å unit cell was difficult even to anticipate and would necessarily be novel. Surely the large Cs^+ ions must remain more distant from the inner surfaces of the zeolite than smaller ions and therefore closer to the centers of the cavities and to each other. The unusually short approaches that must occur, unless they are destabilizing enough to prevent the formation of Cs_{12}–A, might impart some interesting properties to this material.

Beginning in 1956, Breck et al. reported that cesium ion exchange into zeolite A with a 100% excess of Cs^+ (0.14 M aqueous solution at 90 °C) resulted in the replacement of only 31% of the Na^+ ions in the structure.[2] Later Barrer et al. increased the level of Cs^+ exchange to 45% by exposing the zeolite to succesive concentrated aqueous solutions at 25 °C.[3] When "adjusted to a standard equilibrium solution strength" of 0.1 M, the level of Cs^+ exchange was calculated to be about 60%, about 7/12.[3,4] A number of attempts made in this laboratory to accomplish full Cs^+ exchange into zeolite A by various ion-exchange strategies have allowed the maximum extent of Cs^+ exchange to increase gradually during the past decade from 7/12 to 11/12.[5-10]

By straightforward exhaustive methods of exchange (an aqueous Cs^+ solution flowed past a single crystal in a capillary), Cs_7Na_5–A,[5] Cs_7K_5–A,[6] and Cs_9Tl_3–A[7] were prepared. It was surprising initially to see these apparent ion-exchange limits. Methods involving the chemical complexation of the leaving cation led to $Cs_{7.3}$-$Ag_{4.7}$–A[8] and $Cs_{8.5}Ag_{3.5}$–A.[9] Even though there appeared to be no fundamental reason why full Cs^+ exchange could not be achieved, the conventional ion-exchange methods, which rely only on the principle of mass action and complexation, were clearly inadequate. This could not be explained by ion sieving[4] because one Cs^+ ion was always found inside each sodalite unit in all of the partially Cs^+-exchanged structures studied.[5-10] Furthermore, the crystal structures clearly demonstrated that exchange limits occurred at compositions where intercationic distances can all remain greater than some limiting value: replacing one more smaller cation with Cs^+ would generate some new substantially shorter Cs^+–Cs^+ contacts. One may surmise that the energy barriers that effectively prevent complete Cs^+ exchange are due to ion crowding.

It was only recently that 10 or more Cs^+ ions per unit cell were exchanged into zeolite A.[10] This involved methods that annihilate the leaving cation, NH_4^+, by reaction with OH^- and resulted in the preparation of $Cs_{10}Na_4(OH)_2$–A and $Cs_{11}X_2(H_3O)(OH)_2$–A (X = an alkali-metal cation), in which hydroxide ions bridge between the closest Cs^+ ions. These hydroxide ions stabilize the high concentration of Cs^+ ions in the cavities of zeolite A, and they are retained even though additional alkali-metal cations must concomitantly remain with the zeolite. This is similar to salt imbibation[11] and can be viewed as overexchange.[12,13]

More recently, the reaction of hydrated $(NH_4^+)_{12}$–A with cesium hydroxide successfully produced Cs_{12}–A·CsOH,[14] zeolite A containing no exchangeable cations other than Cs^+ but with one extra molecule of cesium hydroxide per unit cell. This hydroxide ion could not be identified crystallographically (the data set was small) but is likely to be located between the two cesium ions in the sodalite unit. An attempt to remove the extra CsOH by heating Cs_{12}–A·CsOH at 350 °C was unsuccessful, probably

(1) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1969**, *B25*, 925–946.
(2) Breck, D. W.; Eversole, W. G.; Milton, R. M.; Reed, T. B.; Thomas, T. L. *J. Am. Chem. Soc.* **1956**, *78*, 5963–5971.
(3) Barrer, R. M.; Rees, L. V. C.; Ward, D. J. *Proc. R. Soc. London, A* **1963**, *273A*, 180–197.
(4) Breck, D. W. *Zeolite Molecular Sieves: Structure, Chemistry, and Use*; Wiley: New York, 1974; pp 537–541.
(5) Vance, T. B., Jr.; Seff, K. *J. Phys. Chem.* **1975**, *79*, 2163–2167.
(6) Firor, R. L.; Seff, K. *J. Am. Chem. Soc.* **1977**, *99*, 6249–6253.
(7) Subramanian, V.; Seff, K. *J. Phys. Chem.* **1979**, *83*, 2166–2169.
(8) Kim, Y.; Seff, K. *Bull. Korean Chem. Soc.* **1984**, *5*, 117–121.
(9) Kim, Y.; Seff, K., unpublished work.
(10) Dejsupa, C.; Seff, K., submitted for publication in *J. Phys. Chem.*
(11) Rabo, J. A. In *Zeolite Chemistry and Catalysis*; Rabo, J. A., Ed.; ACS Monograph 171; American Chemical Society: Washington DC, 1976; pp 332–349.
(12) McCusker, L. B.; Seff, K. *J. Am. Chem. Soc.* **1978**, *100*, 5052–5057.
(13) Ronay, C.; Seff, K. *J. Phys. Chem.* **1985**, *89*, 1965–1970.
(14) (a) Heo, N. H.; Dejsupa, C.; Seff, K. *J. Phys. Chem.* **1987**, *91*, 3943–3944. (b) Dejsupa, C.; Heo, N. H.; Seff, K. *J. Phys. Chem.* **1987**, *91*, 3943–3944.

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because the hot cesium hydroxide was corrosive to the zeolite framework.

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

$$Na_{12}\text{-}A + 12Cs^0 \rightarrow Cs_{12}\text{-}A + 12Na^0$$

would be positive enough to provide an important additional driving force toward complete exchange. The following ΔE values, not involving the zeolite, are readily calculated.[15]

$$Cs(s) + Na^+ \rightarrow Cs^+ + Na(s) \qquad \Delta E_{aq}{}^\circ = +0.21\ V$$

$$Cs(g) + Na^+ \rightarrow Cs^+ + Na(g) \qquad \Delta E_{aq}(25\ ^\circ C) = +0.41\ V$$

The ΔE value for the latter reaction was calculated with vapor pressures of 1.0×10^{-1} Torr for pure Cs^0 at 209 °C and 2.3×10^{-8} Torr for Na^0 at the same temperature. (Its mole fraction in the Cs(l) should be very small and was approximated to be 1.0×10^{-4} by considering the amounts of Cs^0 used and Na^0 produced by reaction with only one crystal of Na_{12}–A.) Calculations to correct this value to actual crystal reaction temperatures have not been done; one may assume that the changes would be small because the heat capacities of the reactants are comparable to those of the products. All reduced sodium atoms should have migrated out of the zeolite lattice and should have distilled away from the crystal's surface, so that a crystal, e.g. at 350 °C, would indeed be in contact with only Cs(g) and Na(g).

This reaction may be viewed as a way of achieving ion exchange without the use of a solvent. If successful, such redox methods of ion exchange might generally allow problems of hydrolysis and overexchange to be circumvented. These problems are often encountered when ion exchange from aqueous solution is attempted.

Experimental Section

Colorless crystals of zeolite 4A (stoichiometry $Na_{12}Si_{12}Al_{12}O_{48}\cdot 27H_2O$; a composition near this with Si/Al ca. 1.04 has been proposed) were prepared by Charnell's method.[16] A single crystal, a cube 0.08 mm on an edge, was lodged in a fine Pyrex capillary on a vacuum line. After complete dehydration at 350 °C (1×10^{-5} Torr) for 2 days,[17] cesium vapor (99.98% purity; Johnson Matthey Inc.) was introduced by distillation from a side-arm break-seal ampule to the glass-tube extension of the crystal-containing capillary. This glass reaction vessel was then sealed off under vacuum and placed within two cylindrical coaxially attached horizontal ovens. 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 first reaction, carried out at 250 °C (ca. 0.1 Torr of cesium vapor) (cesium source at 209 °C[18]) for 16 h, resulted in incomplete reaction (crystal 1). A second crystal of Na_{12}–A was prepared similarly and allowed to react at a higher temperture, 350 °C (ca. 0.1 Torr of cesium vapor), for 16 h (crystal 2). The resulting black crystals were sealed off from the reaction vessel by torch after cooling to room temperature. A third crystal (crystal 3) was prepared as crystal 2 was but was then heated at 450 °C (1×10^{-5} Torr) for 4 days to ensure that all of the reduced sodium metal had distilled from its surface. The true color of the crystal could certainly then be seen under the microscope; like crystals 1 and 2, it was black and lusterous.

A Syntex four-circle computer-controlled diffractometer with a graphite monochromator and a pulse-height analyzer was used for preliminary experiments and for the subsequent collection of diffraction intensities, all at 24 (1) °C. Molybdenum radiation ($K\alpha_1$, λ = 0.709 30 Å; $K\alpha_2$, λ = 0.713 59 Å) was used throughout.

Diffraction data for the "b" reflections of the $Fm3c$ superstructure of crystal 3 were carefully examined at a scan rate of 0.25° min^{-1} with a scan/background time ratio of 1.0 in the range of $2° \leq 2\theta \leq 25°$. Only one reflection (1, 3, 5) had an intensity above its 3σ level. This indicates substantially less b reflection intensity than is usually observed for zeolite A.[19] For this reason, as well as for others discussed previously,[20,21] $Pm3m$ was used instead of $Fm3c$ throughout this work.

In each case, the cell constant, a = 12.252 (1), 12.279 (1), and 12.276 (1) Å for crystals 1–3, respectively, was determined by a least-squares treatment of 15 intense reflections for which $18° < 2\theta < 30°$. The θ–2θ scan technique was used for data collection. Each reflection was scanned at a constant rate of 1.0° min^{-1} from 1° (in 2θ) below the calculated $K\alpha_1$ peak to 1° 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 in diverse regions of reciprocal space were recorded every 47 reflections to monitor crystal and instrument stability. Only small random fluctuations of these check reflections were observed during the course of data collection. The intensities of all lattice points for which $2\theta < 70°$ were recorded.

For crystals 1 and 2, standard deviations were assigned to individual reflections by

$$\sigma(I) = [\omega^2(CT + B_1 + B_2) + (pI)^2]^{1/2}$$

where CT is the total integrated count, B_1 and B_2 are the background counts, and I is the intensity. The value of p = 0.02 was found to be appropriate for the instrumentation used.[22] The intensities were corrected for Lorentz and polarization effects; the contribution of the monochromator crystal was calculated assuming it to be half-perfect and half-mosaic in character.

For crystal 3, reflections from two intensity-equivalent regions of reciprocal space (hkl, $h \leq k \leq l$; hkl, $k \leq l \leq h$) were similarly examined. The raw data from each region were corrected for Lorentz and polarization effects including that due to incident beam monochromatization; the reduced intensities were merged, and the resultant estimated standard deviations were assigned to each averaged reflection by the computer program COMPARE.[23] Other details regarding data reduction have been discussed previously.[24,25]

Absorption corrections ($\mu R \sim 0.35$) were judged to be negligible for all crystals.[26] An empirical ψ scan examination of crystal 3 (Cs_{12}–A·$^1/_2$Cs) showed only negligible fluctuations in intensity for three reflections. Only those reflections in each final data set for which the net count exceeded 3 times its standard deviation were used in structure solution and refinement. This amounted to 227, 201, and 360 reflections for crystals 1–3, respectively.

Structure Determination

$Cs_{8.5}Na_{3.5}$–A·$^1/_2$Cs (Crystal 1). Full-matrix least-squares refinement was initiated with the atomic parameters of the framework atoms [(Si, Al), O(1), O(2), and O(3)] and Cs^+ ions at Cs(1), Cs(2), and Cs(3) of $Cs_{11}Ca_{0.5}$–A·$^1/_2$Cs.[27] This model converged to $R_1 = \sum|F_o - |F_c||/\sum F_o = 0.11$ and $R_2 = (\sum w(F_o - |F_c|)^2/\sum wF_o^2)^{1/2} = 0.10$ with occupancies of 3.08 (8), 4.31 (1), and 1.61 (8) for Cs(i), i = 1–3, respectively. These values suggested the presence of unreacted Na^+ ions at Na(1) on threefold axes. These were found on a Fourier function, and their inclusion reduced the error indices to R_1 = 0.072 and R_2 = 0.060. A subsequent Fourier function revealed some electron density at Cs(4), at (0.32, 0.32, 0.5). Allowing all Cs(i) occupancies to vary except that at Cs(1), which was not permitted to exceed 3.0 (its maximum value by symmetry), and allowing all anisotropic thermal parameters to vary except for that at Cs(4), which was refined isotropically, led to R_1 = 0.064 and R_2 = 0.043, with converged occupancies given in the last column of Table Ia. The unusually large thermal parameter of Cs(4), 43 (9) Å^2, suggested that the z coordinate of Cs(4) should be allowed to refine off the mirror plane at 0.5. This was done, and in a refinement with all positional and thermal parameters free to vary, except that the

(15) *Handbook of Chemistry and Physics*, 64th ed.; Chemical Rubber Co.: Cleveland, 1983; pp D157–D158.
(16) Charnell, J. F. *J. Cryst. Growth* **1971**, *8*, 192–194.
(17) Subramanian, V.; Seff, K. *J. Phys. Chem.* **1977**, *81*, 2249–2251.
(18) Reference 15, pp D215–D218.
(19) McCusker, L. B.; Seff, K. *J. Am. Chem. Soc.* **1981**, *103*, 3441–3446.
(20) Cruz, W. V.; Leung, P. C. W.; Seff, K. *J. Am. Chem. Soc.* **1978**, *100*, 6997–7003.
(21) Seff, K.; Mellum, M. D. *J. Phys. Chem.* **1984**, *88*, 3560–3563.
(22) Peterson, S. W.; Levy, H. A. *Acta Crystallogr.* **1957**, *10*, 70–76.
(23) The following are principal computer programs used in this study. Data reduction: Ottersen, T. COMPARE; University of Hawaii, 1973. Ottersen, T. LP-76; University of Hawaii, 1976. Full-matrix least-squares: Gantzel, P. K.; Sparks, R. A.; Trueblood, K. N. UCLA LS4; American Crystallographic Association Program Library (old), No. 317 (modified). Fourier: Hubbard, C. R.; Quicksall, C. O.; Jacobson, R. A. ALFF; Ames Laboratory Fast Fourier: Iowa State University, 1971. Plotting: Johnson, C. K. ORTEP, Report No. ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.
(24) Seff, K. *Acc. Chem. Res.* **1976**, *9*, 121–128.
(25) Firor, R. L.; Seff, K. *J. Am. Chem. Soc.* **1977**, *99*, 4039–4044.
(26) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. II, p 132.
(27) Heo, N. H. Ph.D. Thesis, University of Hawaii, 1987.

Table I. Positional, Thermal, and Occupancy Parameters[a] of Cs_xNa_{12-x}–A·$^1/_2$Cs, x = 8.5 or 12

	Wyckoff position	x	y	z	β_{11}[b] or B_{iso}[c]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	occupancy[d] fixed	occupancy[d] varied
					(a) $Cs_{8.5}Na_{3.5}$–A·$^1/_2$Cs, Crystal 1							
(Si, Al)	24 (*k*)	0	1830 (3)	3709 (3)	21 (3)	22 (3)	11 (3)	0	0	10 (5)	24[e]	
O(1)	12 (*h*)	0	2220 (11)	5000[f]	95 (17)	24 (12)	19 (12)	0	0	0	12	
O(2)	12 (*i*)	0	2960 (10)	2960 (10)	52 (14)	36 (8)	36 (8)	0	0	22 (24)	12	
O(3)	24 (*m*)	1129 (5)	1129 (5)	3385 (8)	29 (5)	29 (5)	78 (12)	5 (14)	16 (11)	16 (11)	24	
Cs(1)	3 (*c*)	0	5000[f]	5000[f]	139 (6)	77 (3)	77 (3)	0	0	0	3	3.08 (8)
Cs(2)	8 (*g*)	2814 (2)	2814 (2)	2814 (2)	55 (2)	55 (2)	55 (2)	11 (4)	11 (4)	11 (4)	4	4.07 (6)
Cs(3)	8 (*g*)	913 (7)	913 (7)	913 (7)	108 (7)	108 (7)	108 (7)	−41 (14)	−41 (14)	−41 (14)	1.5	1.62 (4)
Na(1)	8 (*g*)	2153 (13)	2153 (13)	2153 (13)	2.7 (5)						3.5	3.6 (3)
Cs(4)	24 (*m*)	3340 (47)	3340 (47)	4620 (68)	10.0[g]						0.5	0.8 (1)
					(b) Cs_{12}–A·$^1/_2$Cs, Crystal 2							
(Si, Al)	24 (*k*)	0	1838 (4)	3718 (4)	24 (4)	16 (3)	11 (4)	0	0	7 (6)	24[e]	
O(1)	12 (*h*)	0	2257 (14)	5000[f]	82 (18)	15 (12)	27 (13)	0	0	0	12	
O(2)	12 (*i*)	0	2944 (10)	2944 (10)	36 (14)	30 (9)	30 (9)	0	0	27 (28)	12	
O(3)	24 (*m*)	1117 (6)	1117 (6)	3428 (10)	24 (6)	24 (6)	55 (12)	10 (16)	1 (12)	1 (12)	24	
Cs(1)	3 (*c*)	0	5000[f]	5000[f]	87 (5)	71 (3)	71 (3)	0	0	0	3	2.99 (4)
Cs(2)	8 (*g*)	2776 (1)	2776 (1)	2776 (1)	50 (1)	50 (1)	50 (1)	17 (3)	17 (3)	17 (3)	7	7.01 (9)
Cs(3)	8 (*g*)	958 (7)	958 (7)	958 (7)	118 (7)	118 (7)	118 (7)	−65 (13)	−65 (13)	−65 (13)	2	2.18 (5)
Cs(4)	12 (*j*)	2716 (45)	2716 (45)	5000[f]	9 (2)						0.5	0.6 (1)
					(c) Cs_{12}–A·$^1/_2$Cs, Crystal 3							
(Si, Al)	24 (*k*)	0	1836 (2)	3720 (2)	20 (2)	18 (2)	12 (2)	0	0	10 (3)	24[e]	
O(1)	12 (*h*)	0	2256 (8)	5000[f]	79 (10)	37 (9)	15 (6)	0	0	0	12	
O(2)	12 (*i*)	0	2956 (5)	2956 (5)	30 (7)	28 (5)	28 (5)	0	0	30 (13)	12	
O(3)	24 (*m*)	1126 (4)	1126 (4)	3429 (7)	34 (3)	34 (3)	42 (6)	17 (9)	20 (7)	20 (7)	24	
Cs(1)	3 (*c*)	0	5000[f]	5000[f]	104 (3)	73 (2)	73 (2)	0	0	0	3	3.13 (3)
Cs(2)	8 (*g*)	2755 (1)	2755 (1)	2755 (1)	47 (1)	47 (1)	47 (1)	11 (1)	11 (1)	11 (1)	7	7.01 (4)
Cs(3)	8 (*g*)	935 (4)	935 (4)	935 (4)	118 (4)	118 (4)	118 (4)	−78 (7)	−78 (7)	−78 (7)	2	2.03 (3)
Cs(4)	12 (*j*)	2963 (30)	2963 (30)	5000[f]	10 (1)						0.5	0.71 (7)

[a] Positional and anisotropic thermal parameters are given ×10^4. Numbers in parentheses are the estimated standard deviations in the units of the least significant figure given for the corresponding parameter. 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] Rms displacements can be calculated from β_{ii} values with the formula $\mu_i = 0.225a(\beta_{ii})^{1/2}$, where a = 12.3 Å. [c] Isotropic thermal parameter (Å^2). [d] Occupancy factors are given as the number of ions per unit cell. [e] Occupancy for (Si) = 12; occupancy for (Al) = 12. [f] Exactly $^1/_2$ by symmetry. [g] This thermal parameter was fixed in least-squares refinement.

occupancies of all atoms and the isotropic thermal parameter of Cs(4) were fixed at the values given in Table Ia. Cs(4) refined to (0.33, 0.33, 0.46) with R_1 = 0.065 and R_2 = 0.052. The final difference function was featureless except for some residual density near Cs(2) deep in the large cavity. See Table II.

The goodness-of-fit, $(\sum w(F_o - |F_c|)^2/(m - s))^{1/2}$, is 2.0; the number of observations, m, is 227, and the number of parameters, s, is 33. The final structural parameters and selected interatomic distances and angles are presented in Tables Ia and III, respectively.

Cs_{12}–A·$^1/_2$Cs (Crystals 2 and 3). Full-matrix least-squares refinement of crystal 2 using the parameters of all framework atoms and Cs^+ ions in crystal 1 except Cs(4) quickly converged to R_1 = 0.061 and R_2 = 0.051. Refinement including Cs(4), which appeared on a subsequent difference function at (0.26, 0.26, 0.5), with an isotropic thermal parameter lowered these to 0.054 and 0.040, respectively, with occupancies of 2.99 (4), 7.01 (9), 2.18 (5), and 0.78 (12) for Cs(i), i = 1–4, and an unusually large thermal parameter for Cs(4). When the thermal parameter and occupancy of Cs(4) were free to vary, while all other occupancies were fixed at their nearest integers, they converged at 8(2) Å^2 and 0.55(7) with negligible changes in the error indices.

Least-squares refinement of crystal 3 yielded an unambiguous structure with occupancies of 3, 7, 2, and 0.5 for the Cs(i) ions, i = 1–4, resulting in the formula Cs_{12}–A·$^1/_2$Cs with final error indices, R_1 = 0.055 and R_2 = 0.042. As had been seen in the refinement of the structure of crystal 2, the inclusion of Cs(4) had a substantial effect on the error indices, reducing them by more than 0.01. Least-squares refinement of this structure to convergence (R_1 = 0.053 and R_2 = 0.041) in the lower space group $Fm3c$ showed no change in the Cs^+ occupancies, indicating that they are not an artifact of the choice of space group. Table II contains final $Pm3m$ Fourier information.

The values for the goodness-of-fit are 1.5 and 2.4, the m's are 201 and 360, and the s's are both 31 for crystals 2 and 3, respectively. Their final structure parameters are presented in Table Ib,c.

Table II. Highest Peaks on Two Final Fourier Functions[a]

position	Fourier cryst 1	Fourier cryst 3	diff Fourier cryst 1	diff Fourier cryst 3
Cs(1)	73.4 (5)	81.4 (5)	0.6 (5)	2.2 (5)
Cs(2)	57.6 (3)	>99.9 (3)[b]	1.0 (3)	3.9 (3)
Cs(3)	17.1 (3)	20.2 (3)	0.1 (3)	0.0 (3)
Cs(4)	3.8 (2)[c]	2.5 (2)[c]	0.2 (2)	0.8 (2)
ca. 0.2, 0.2, 0.2	12.9 (3)[d]	3.6 (3)[e,f]	1.0 (3)	1.3 (3)
ca. 0.3, 0.3, 0.3[g]	4.4 (3)[h]	2.7 (1)[i]	1.1 (3)	1.4 (1)
0.5, 0.5, 0.5	4.8 (8)		1.1 (8)	

[a] Peak heights (e/Å^3). Esd's are given in parentheses. The esd at a general position is about 0.12 e/Å^3 for all three crystals. [b] The peak height is about 112 e/Å^3. [c] Although this peak was not high, its addition to least-squares lowered R values appreciably and its occupancy remained significant. [d] 0.2153, 0.2153, 0.2153. [e] Although this peak has moderate height, its occupancy refined to zero in least squares. It is midway between the high Cs(2) and Cs(3) peaks and may be attributed to termination-of-series error. Also, an ion at this position would be impossibly near (about 2.0 Å) a Cs^+ ion. [f] 0.227, 0.227, 0.227. [g] Very near Cs(2). [h] 0.28, 0.28, 0.34. [i] 0.27, 0.31, 0.34.

All shifts in the final cycles of least-squares refinement for all three crystals were less than 0.1% of their corresponding standard deviations. Interactomic distances and angles are given in Table III.

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 of σ, its standard deviation. Atomic scattering factors for Cs^+, Na^+, O^-, and (Si, Al)$^{1.75+}$ were used.[28,29]

(28) Doyle, P. A.; Turner, P. S. *Acta Crystallogr., Sect. A: Cryst. Phys. Diffr., Theor. Gen. Crystallogr.* **1968**, *24*, 390–397.
(29) Reference 26, Vol. IV, pp 73–87.

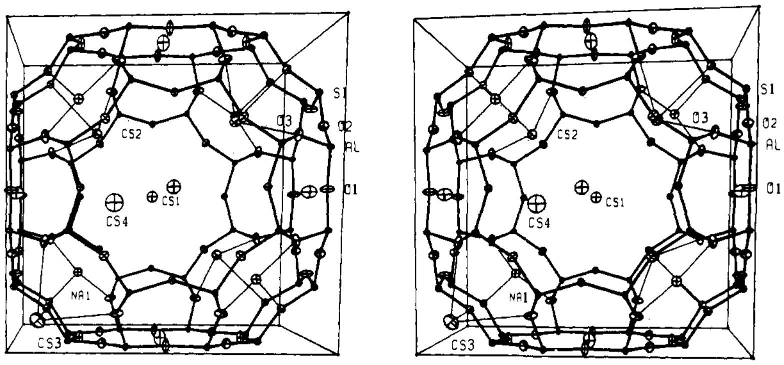

Figure 1. Stereoview of a large cavity in Cs_8Na_4–A. The zeolite A framework is drawn with heavy bonds between oxygen atoms and tetrahedrally coordinated (Si, Al). Cation coordination by framework oxygens is indicated by fine lines. Cs^+ ions are relatively far from 6-ring planes, while Na^+ ions are almost at their centers. Ellipsoids of 20% probability are shown.

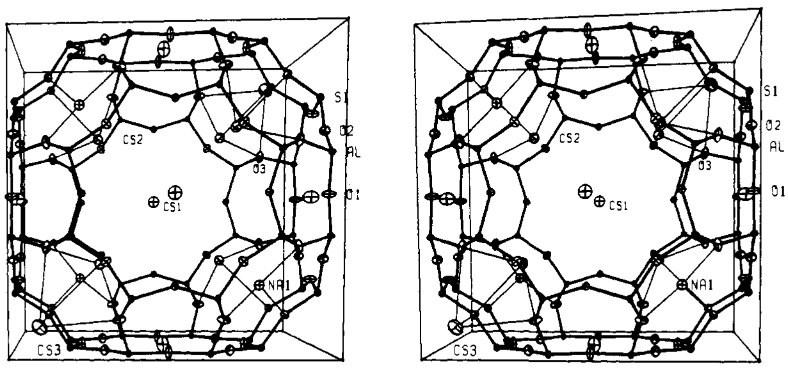

Figure 2. Stereoview of a large cavity in Cs_9Na_3–A·Cs (or $Cs_{10}Na_3$–A). See the caption to Figure 1 for other details.

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 (f') of the anomalous dispersion correction.[30,31]

Crystallographic Results

In all three structures, Cs^+ ions are found at four crystallographic sites as summarized in Table IV. These structures differ only in the occupancies at Cs(2) and Cs(3), in the z coordinate of Cs(4) opposite a 4-ring, and in the presence of unreacted Na^+ ions in crystal 1.

In each structure, three Cs^+ ions at Cs(1) fill the equipoints of symmetry C_{4h} (D_{4h} in $Pm3m$) at the centers of the 8-rings, as they have in all previously reported Cs^+-exchanged zeolite A structures.[4-10] Each Cs(1) cation is ca. 3.38 (1) Å from four O(1) oxygens and ca. 3.55 (1) Å from four O(2)'s (see interatomic distances in Table III). 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.[32,33]

$Cs_{8.5}Na_{3.5}$–A·$^1/_2$Cs. The structure of $Cs_{8.5}Na_{3.5}$–A·$^1/_2$Cs can perhaps best be viewed as having two kinds of 12.3-Å "unit cells", of composition Cs_8Na_4–A and Cs_9Na_3–A·Cs (see Table IV for the distribution of Cs^+ ions in $Cs_{8.5}Na_{3.5}$–A·$^1/_2$Cs). Possible atomic arrangements in the large cavities of Cs_8Na_4–A and Cs_9Na_3–A·Cs are shown in Figures 1 and 2, respectively. In Cs_8Na_4–A, four unreacted Na^+ ions are placed tetrahedrally about the large cavity. Each Na^+ ion extends 0.58 Å into the large cavity from the [111] plane at O(3) and coordinates to three O(3) oxygens at 2.33 Å. Three Cs^+ ions at Cs(2) are on threefold axes in the large cavity opposite 6-rings. Each is 3.00 (1) Å from the three O(3) oxygens of its 6-ring and 1.98 Å from the [111] plane at O(3). A remaining 6-ring is occupied by one Cs^+ ion at Cs(3) on a threefold axis in the sodalite unit. It is 3.05 (2) Å from three O(3) oxygens and is 2.05 Å from its [111] plane at O(3). Another Cs^+ ion at Cs(4) is located opposite a 4-ring, the usual position for the 12th

Table III. Selected Interatomic Distances (Å) and Angles (deg) for Cs_xNa_{12-x}–A·$^1/_2$Cs, x = 8.5 or 12[a]

	$Cs_{8.5}Na_{3.5}$–A·$^1/_2$Cs (crystal 1)	Cs_{12}–A·$^1/_2$Cs (crystal 2)	Cs_{12}–A·$^1/_2$Cs (crystal 3)
(Si, Al)–O(1)	1.653 (6)	1.656 (7)	1.654 (4)
(Si, Al)–O(2)	1.661 (5)	1.658 (5)	1.664 (3)
(Si, Al)–O(3)	1.676 (4)	1.670 (4)	1.673 (2)
Cs(1)–O(1)	3.406 (14)	3.369 (17)	3.368 (10)
Cs(1)–O(2)	3.535 (17)	3.570 (2)	3.548 (9)
Cs(2)–O(2)	3.457 (3)	3.422 (2)	3.400 (1)
Cs(2)–O(3)	3.003 (10)	2.991 (11)	2.946 (6)
Cs(3)–O(2)	3.719 (19)	3.422 (9)	3.691 (10)
Cs(3)–O(3)	3.052 (15)	3.045 (15)	3.080 (9)
Cs(4)–O(1)	4.319 (72)	3.382 (43)	3.350 (43)
Cs(4)–O(3)	4.096 (85)	3.382 (45)	3.335 (44)
Na(1)–O(3)	2.330 (11)		
Cs(1)–Cs(2)	5.122 (1)	5.151 (1)	5.161 (4)
Cs(1)–Cs(4)	4.586 (26)	4.357 (5)	4.353 (4)
Cs(2)–Cs(2)	5.356 (6)	5.461 (4)	5.513 (2)
Cs(2)–Cs(3)	4.034 (17)	3.867 (15)	3.868 (8)
Cs(3)–Cs(3)	3.875 (32)	4.076 (30)	3.978 (16)
Cs(3)–Cs(4)	6.171 (87)	5.826 (31)	5.849 (28)
O(1)–(Si, Al)–O(2)	106.7 (8)	106.9 (6)	106.1 (5)
O(1)–(Si, Al)–O(3)	112.0 (4)	111.5 (5)	111.4 (3)
O(2)–(Si, Al)–O(3)	107.3 (4)	108.2 (4)	108.1 (3)
O(3)–(Si–Al)–O(3)	111.2 (5)	110.3 (6)	111.5 (4)
(Si, Al)–O(1)–(Si, Al)	146.4 (9)	143.8 (11)	143.7 (7)
(Si, Al)–O(2)–(Si, Al)	157.1 (11)	159.9 (4)	158.6 (7)
(Si, Al)–O(3)–(Si, Al)	142.3 (7)	145.6 (8)	144.7 (4)
O(3)–Cs(2)–O(3)	81.2 (3)	84.3 (3)	85.5 (2)
O(3)–Cs(3)–O(3)	79.7 (4)	82.5 (4)	81.0 (2)
O(3)–Na(1)–O(3)	114.1 (5)		
Cs(2)–Cs(3)–Cs(3)	180.0	180.0	180.0

[a] The numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding parameter.

(30) Cromer, D. T. *Acta Crystallogr.* **1965**, *18*, 17–23.
(31) Reference 26, Vol. IV, pp 149–150.
(32) Ogawa, K.; Nitta, M.; Aomura, K. *J. Phys. Chem.* **1978**, *82*, 1665–1670.
(33) Takaishi, T.; Hosoi, H. *J. Phys. Chem.* **1982**, *86*, 2089–2094.

Table IV. Distribution of Cs^+ Ions in Fully Dehydrated, Fully and Partially Cs^+-Exchanged Zeolite A

crystal no.	overall formula: components	no. of Cs^+ ions: in 8-rings, Cs(1)	opposite 6-rings in the α-cage,[a] Cs(2)	opposite 6-rings in the β-cage,[a] Cs(3)	opposite 4-rings, Cs(4)	total
1	$Cs_{8.5}Na_{3.5}$–A·1/2Cs:	3	4	1.5	0.5[b]	9
	Cs_8Na_4–A	3	3	1	1[b]	8
	Cs_9Na_3–A·Cs	3	5	2	0	10
2, 3	Cs_{12}–A·1/2Cs:	3	7	2	0.5	12.5
	Cs_{12}–A	3	6	2	1	12
	Cs_{12}–A·Cs	3	8	2	0	13

[a] The α-cage is the large cavity. The β-cage is the sodalite unit. [b] Nearly opposite a 4-ring, at Wyckoff position 24 (m).

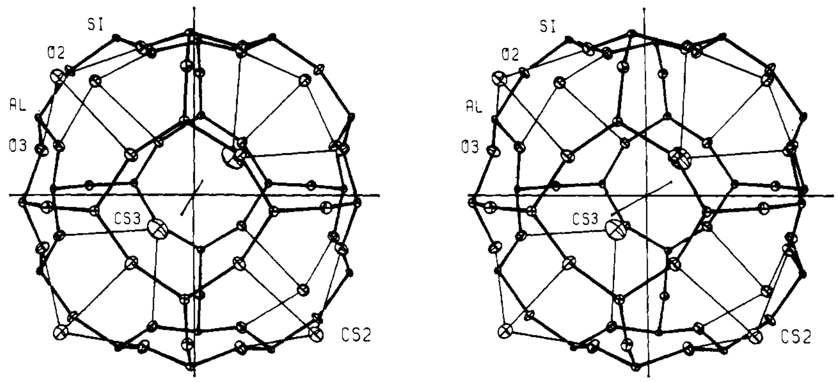

Figure 3. Stereoview of a sodalite cavity in Cs_{12}–A. See the caption to Figure 1 for other details.

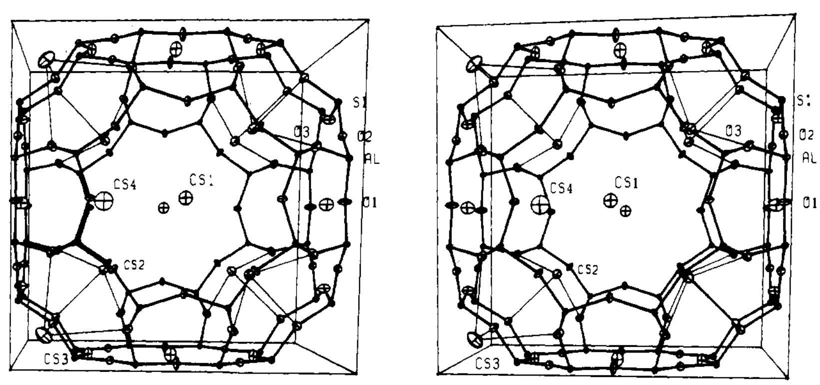

Figure 4. Stereoview of a large cavity in Cs_{12}–A. See the caption to Figure 1 for other details.

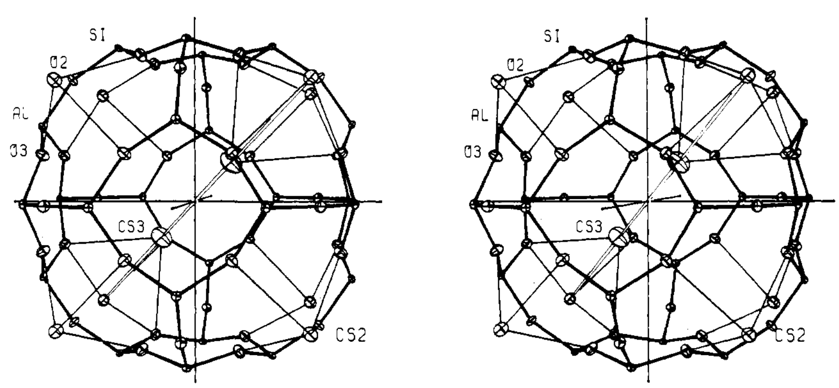

Figure 5. Stereoview of a sodalite cavity in Cs_{12}–A·Cs (or Cs_{13}–A). See the caption to Figure 1 for other details.

large monopositive ion. This Cs^+ ion is rather far from framework oxygens (4.10 (9) Å from O(3)) probably because of repulsive interaction with the Na^+ ion in an adjacent 6-ring. (Also, less importantly, this distance may be virtual, a bit too long: This particular 4-ring may have a distorted geometry due to the presence of its Cs^+ ion.) When this Na^+ is removed by further redox reaction, the 4-ring Cs^+ ion can get closer to the framework, as shown in the unit cell of Cs_{12}–A (vide infra).

It is quite surprising to note, from their approach distances to framework oxygens, that all 13 cesiums and sodiums in the remaining half of the unit cells of $Cs_{8.5}Na_{3.5}$–A·$^1/_2$Cs appear to be cations: that is, Cs_9Na_3–A·Cs appears to be $Cs_{10}Na_3$–A. With three Na^+ ions in 6-rings, each unit cell contains seven Cs^+ ions located on the threefold axes: five in the large cavity and two in the sodalite unit opposite 6-rings (see Table IV). The only way to place ten ions in the eight 6-rings per unit cell is to have two such rings each accommodate two ions. Therefore, two rings are each occupied by two Cs^+ ions, one at Cs(2) and one at Cs(3), 4.03 (2) Å apart on the same threefold axis, one on each side of the 6-ring. The second ion at Cs(3) (opposite a 6-ring in the

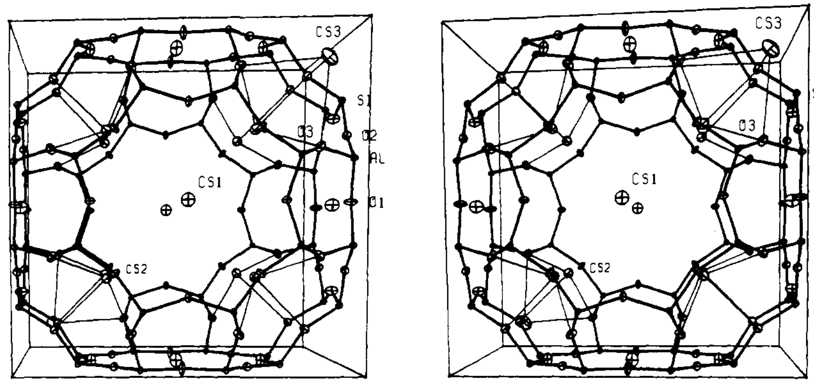

Figure 6. Stereoview of a large cavity in Cs_{12}–A·Cs (or Cs_{13}–A). See the caption to Figure 1 for other details.

sodalite unit) must be placed as far as possible from the first one to minimize their intercationic repulsive interaction; even so, it is only 3.88 (3) Å away. It follows, therefore, that all four Cs^+ ions lie on the same threefold axis. These short inter-cesium distances describe isolated linear $(Cs_4)^{3+}$ cations, Cs(2)–Cs(3)–Cs(3)–Cs(2) (vide infra).

Cs_{12}–A·$^1/_2$Cs. Cs^+ ions occupy four crystallographically distinct sites, as summarized in Table IV. The atomic arrangements in crystal 3, taken as representative, are shown in Figures 3–6. Crystal 2 has the same structure as crystal 3.

In addition to the three Cs^+ ions at the centers of the 8-rings, each large cavity contains 7 Cs^+ ions at Cs(2) and 0.5 at Cs(4). Each sodalite cage contains two Cs^+ ions at Cs(3) opposite 6-rings. These are placed on the same threefold axis on opposite sides of the origin 4.08 (3) and 3.98 (2) Å apart, respectively, for crystals 2 and 3. These short distances are exemplary of the ion crowding, which was anticipated for Cs–A. Cs_{12}–A·$^1/_2$Cs may also best be discussed as having two kinds of 12.3-Å unit cells, Cs_{12}–A and Cs_{13}–A in this case.

In Cs_{12}–A, two adjacent 6-rings of 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 that connects those two 6-rings. Six large-cavity Cs^+ ions fill the remaining six 6-rings. Each is 2.99 (1) Å from three O(3) oxygens and 1.89 Å from the [111] plane at O(3) for crystal 2; these values are 2.95 (1) and 1.83 Å for crystal 3. The large-cavity and sodalite-cavity views of Cs_{12}–A are shown in Figures 3 and 4, respectively.

In Cs_{13}–A, all eight threefold axis sites in the large cavity are occupied by Cs^+ ions at Cs(2), so no 4-ring sites are available. Again, the two Cs^+ ions in the sodalite unit must share a threefold axis with two of these eight Cs^+ ions at Cs(2) with inter-cesium distances of 3.87 (2) Å (Cs(2)–Cs(3)) and 4.08 (3) Å (Cs(3)–Cs(3)) for crystal 2 and 3.87 (1) and 3.98 (2) Å, respectively, for crystal 3. The large-cavity and sodalite-cavity views are presented in Figures 5 and 6, respectively.

If the electrons of the extra cesium atoms are viewed as being delocalized only among the closest Cs^+ ions, one may recognize isolated linear cesium clusters, $(Cs_4)^{3+}$, Cs(2)–Cs(3)–Cs(3)–Cs(2) (Figure 7).

Cesium reacts with dehydrated Ca_6–A and K_{12}–A to give the same (or nearly the same) product, Cs_{12}–A·$^1/_2$Cs. Crystals of intermediate composition were also prepared from Ca_6–A as in this work. With less certainty, Co_4Na_4–A appears to react to give Cs_{12}–A·$^1/_2$Cs also. These results[27] will be presented in subsequent reports.

Discussion

Fully Cs^+-exchanged, fully dehydrated zeolite A, Cs_{12}–A·$^1/_2$Cs, has been synthesized by the reduction of the Na^+ ions in Na_{12}–A with ca. 0.1 Torr of cesium vapor at 350 °C. The intermediate composition $Cs_{8.5}Na_{3.5}$–A·$^1/_2$Cs formed upon reaction at 250 °C.

In the crystal structures of Cs_xNa_{12-x}–A·$^1/_2$Cs, whether x is 8.5 or 12, 0.5 extra cesium was found per unit cell. Each of these atoms associates with three Cs^+ ions to form $(Cs_4)^{3+}$ (see Figure 7). The condensation of three Cs^+ ions into a relatively small volume of space, as the cesium atom involved allows, apparently

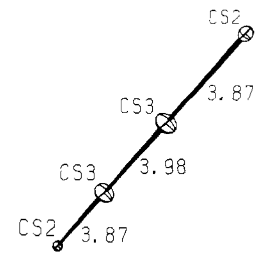

Figure 7. Linear cesium cluster, $(Cs_4)^{3+}$, on a threefold axis passing through the sodalite cavities of Cs_9Na_3–A·Cs and Cs_{12}–A·Cs. Bond lengths are in angstroms. Ellipsoids of 20% probability are shown.

leads to a lowering of the net electrostatic repulsive energy among the cesium species as compared to that in $Cs_{8.5}Na_{3.5}$–A and in Cs_{12}–A. In addition, some covalent bonding has been introduced among the cesiums. The extra cesium atoms found in $(Cs_4)^{3+}$ of $Cs_{8.5}Na_{3.5}$–A·$^1/_2$Cs indicate that full Cs^+-exchange is not required for extra cesium to be sorbed. Rather, it is at some intermediate level of exchange that the concentration of Cs^+ ions and the degree of ion-crowding is sufficient to cause the zeolite to sorb extra Cs atoms.

Alternatively, Cs_{12}–A·$^1/_2$Cs and $Cs_{8.5}Na_{3.5}$–A·$^1/_2$Cs may be viewed as materials with 12.5 ions and 0.5 excess electron per unit cell. The Cs^+ ions in Cs_{12}–A·$^1/_2$Cs form a three-dimensional array with inter-cesium distances of 3.87 (1), 3.98 (2), 4.35 (1), 5.16 (1), and 5.51 (1) Å for Cs(2)–Cs(3), Cs(3)–Cs(3), Cs(1)–Cs(4), Cs(1)–Cs(2), and Cs(2)–Cs(2), respectively (distances from the structure of crystal 3). These are shorter than or comparable to those in Cs metal (5.31 Å).[34] Therefore, the excess electrons may form a metallic continuum of electron density, encompassing the entire volume of the single crystal of zeolite A. To test this alternative, a freshly prepared powdered sample of Cs_{12}–A·$^1/_2$Cs was examined within its Pyrex container under vacuum. The sample was placed in the field of an oscillating circuit; the simple instrument used is sometimes called a metal detector or a grip dip meter. The eddy currents, which would be induced in a metal, would drain energy from this field. In a wide range of frequency, no noticeable energy loss was detected with Cs_{12}–A·$^1/_2$Cs, although positive results were achieved with powders of aluminum or graphite. This suggests that the excess electrons are localized among the closest Cs^+ ions, those of the $(Cs_4)^{3+}$ clusters.

It appears that the intermediate product $Cs_{8.5}Na_{3.5}$–A·$^1/_2$Cs is the result of incomplete reaction due to slow diffusion kinetics within the zeolite at 250 °C; it seems unlikely that a temperature difference of only 100 °C would cause this mixed-ion composition to be the thermodynamically stable one. Nonetheless, note that Na^+ ions and Cs atoms coexist within this crystal. That they have not reacted indicates that the chemical activity of the Cs atoms are diminished by their incorporation into $(Cs_4)^{3+}$ clusters.

The $(Cs_4)^{3+}$ cluster can be considered to be a one-dimensional particle-in-a-box system of four linearly arranged Cs^+ ions with

(34) *Interatomic Distances, Supplement*; The Chemical Society: London, 1965; p S-5s.

one electron delocalized among them. The length of this box, 15.4 Å, is approximated by the sum of the three bond lengths plus twice the ionic radius of Cs^+. A broad absorptive transition ($1 \rightarrow 4$) is allowed near the middle of the visible range at about 5220 Å, which could account for the black color of the $(Cs_4)^{3+}$-containing crystals.

At 350 °C, all Na^+ ions in Na_{12}–A were reduced and replaced by Cs^+ ions; this solvent-free ion-exchange reaction went to completion. Simultaneously, no evidence for reaction with the zeolite framework was observed at the temperatures used in this work. This is consistent with the highly positive values of $\Delta G°$ for the reactions of Al_2O_3 or SiO_2 with cesium and is verified experimentally by the very strong diffraction pattern of the resulting zeolite crystal. It is further indicated by the observation that the colorless appearance of the crystal can be restored simply by exposure to the atmosphere; particles of Al or Si, if they had been generated and were responsible for the black color of the crystal, would probably not be easily oxidized.

Several additional experimental observations have been made. When crystals of Cs_{12}–A·$^1/_2$Cs were maintained under vacuum at a temperature above 650 °C, a colorless transparent layer developed very slowly to a thickness of ca. 5 μm. Even after the crystal was heated at 850 °C for 2 days, the black interior of the crystal was still seen without noticeable change in the thickness of the transparent layer. This could indicate that Cs_{12}–A·$^1/_2$Cs decomposes to transparent crystalline Cs_{12}–A by losing its extra cesium atoms. Heating to 1000 °C confirms this; all of the excess cesium atoms are lost, yielding Cs_{12}–A (with three, seven, and two Cs^+ ions at Cs(i), i = 1–3, respectively), which is colorless as expected. These topics will be presented in a subsequent report.[35]

Cs_{12}–A is remarkably stable. Na_{12}–A is stable only to about 750 °C in air[36] or under vacuum. Stabilities up to about 825 °C are found in K_{12}–A and in nearly fully Ca^{2+}-exchanged zeolite A.[36]

After the crystal was heated at 650 °C for 7 days, the interior of the crystal became dark green. This may indicate that some small amount of the green sub-oxide Cs_3O[37] had formed. Note that the uptake of excess Cs^0 by Cs_2O to form Cs_3O is like that by $Cs_{8.5}Na_{3.5}$–A and Cs_{12}–A to form $(Cs_4)^{3+}$-containing zeolites A. Cs_2O[38] must also be considered a cationally crowded material.

It has also been observed that, upon exposure to the atmosphere, the black Cs_{12}–A·$^1/_2$Cs crystal became colorless along a well-defined retreating front over a period of 2 weeks as the atmosphere slowly diffused into an 80-μm crystal. This may be ascribed to a reaction between the excess cesium within the crystal and water or oxygen diffusing into the crystal from the surface, to produce colorless cesium hydroxide (and hydrogen) or cesium oxide, respectively.

Recent ^{29}Si MAS NMR work[39] indicates that the zeolite A framework contains about 3 or 4% more Si than Al. If that is true, the crystallographic results reported here would need to be interpreted somewhat differently. Unit cells of composition $Cs_{11}Si_{13}Al_{11}O_{48}$ and $Cs_{12}Si_{12}Al_{12}O_{48}$ would need to be considered for crystals 2 and 3 (for example) prior to cesium atom absorption. $Cs_{12}Si_{12}Al_{12}O_{48}$ would certainly have sorbed a full cesium atom per unit cell to give $Cs_{12}Si_{12}Al_{12}O_{48}$·Cs, but the present crystallographic results are only marginally consistent at best with the proposition either that $Cs_{11}Si_{13}Al_{11}O_{48}$ would sorb a cesium atom or that it would not. (If it did, only $(Cs_2)^+$ clusters like that shown in Figure 3 could exist in sodalite units of this composition due to packing considerations.) (Such an analysis might resolve a difficult point in the present interpretation: $Cs_{12}Si_{12}Al_{12}O_{48}$ sorbs only 0.5 Cs^0 per unit cell; if half of the unit cells sorb Cs^0, we must ask why the remaining half does not. Various kinetic or equilibrium (packing) arguments might be proposed.) In recent work awaiting publication, Cs_{12}–A·$^3/_4$Cs appears to be the composition of a product, and this could, but need not be, interpreted to give the composition indicated by Blackwell et al.[39] However, the packing constraint on the occupancies, $G_{Cs(2)} + 2G_{Cs(4)} \leq 8$ for crystals 2 and 3, does not allow the present composition to be interpreted as Cs_{12}–A·$^3/_4$Cs. In any event, half or more of the unit cells in Cs_{12}–A·$^1/_2$Cs are of composition $Cs_{12}Si_{12}Al_{12}O_{48}$·Cs, and each contains a linear $(Cs_4)^{3+}$ cluster. The remainder may be $Cs_{12}Si_{12}Al_{12}O_{48}$, $Cs_{11}Si_{13}Al_{11}O_{48}$, or $(Cs_2)^+$-containing $Cs_{12}Si_{13}Al_{11}O_{48}$.

Acknowledgment. We are indebted to the University of Hawaii Computing Center.

Registry No. Cs, 7440-46-2; $NaSiAlO_4$, 12003-51-9; Cs_{12}-A, 12003-48-4; Cs_8Na_4-A, 110826-62-5; Cs_9Na_3-A·Cs, 110874-05-0; Cs_{12}-A·Cs, 110903-50-9.

Supplementary Material Available: Table of observed and calculated structure factors for fully dehydrated, fully or partially Cs^+-exchanged zeolite A, Cs_xNa_{12-x}–A·$^1/_2$Cs, x = 8.5 or 12 (7 pages). Ordering information is given on any current masthead page.

(35) Heo, N. H.; Seff, K. *J. Chem. Soc., Chem. Commun.* **1987**, 1225–1226.

(36) Reference 4, p 495.

(37) (a) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Oxford University: New York, 1984; pp 536–537. (b) Simon, A. In *Structure and Bonding*; Dunitz, J. D., Goodenough, J. B., Hemmerich, P., Ibers, J. A., Jørgensen, C. K., Neilands, J. B., Reinen, D., Williams, R. J. P., Eds.; Springer-Verlag: Berlin, Heidelberg, 1979; Vol. 36, p 112.

(38) Tasi, K. R.; Harris, P. M.; Lassettre, E. N. *J. Phys. Chem.* **1956**, *60*, 338–344.

(39) Blackwell, C. S.; Pluth, J. J.; Smith, J. V. *J. Phys. Chem.* **1985**, *89*, 4420–4422.