Zero-Coordinate Rb^+. The Dehydrated and Hydrated Crystal Structures of Eleven-Twelfths Rubidium-Exchanged Zeolite A

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Abstract: The crystal structures of vacuum-dehydrated (a = 12.261 (2) Å) and hydrated (a = 12.321 (3) Å) $^{11}/_{12}$ Rb^+-exchanged synthetic molecular sieve zeolite A have been determined by single-crystal x-ray diffraction techniques in the cubic space group $Pm3m$. The structures were refined to final R (weighted) indices of 0.055 for dehydrated $Rb_{11}Na$-A and 0.100 for hydrated $Rb_{11}Na$-A. In the dehydrated structure, three equivalent Rb^+ ions lie at the centers of the oxygen 8-rings, while five equivalent Rb^+ ions lie on threefold axes opposite 6-rings in the large cavity. The three remaining Rb^+ ions are nonequivalent, and lie on one unique threefold axis. Two of these are located in the sodalite unit on opposite sides of the origin. *The remaining Rb^+ ion on this threefold axis is 4.35 Å from the nearest ion or atom, a 6-ring oxygen. This Rb^+ ion lies deep within the large cavity and can be considered zero-coordinate by a distance criterion; its shortest approach to another ion exceeds the sum of the appropriate ionic radii by more than 1.5 Å.* This situation has occurred because insufficient sites are available on the inner surface of the zeolite to accommodate all of the large cations present-by difference, one Rb^+ ion per unit cell must occupy a site remote from the anionic zeolite framework. According to the Laplace equation, $\nabla^2 V = 0$, the existence of a potential energy minimum at this site cannot be explained by any purely electrostatic model. In the hydrated structure, five Rb^+ ions are found inside the large cavity on the threefold axes near the 6-oxygen rings; three more lie in the 8-oxygen ring, two somewhat off the plane and one in the plane; two are located inside the sodalite unit; the 11th lies in the large cavity near a 4-oxygen ring. Four water molecules bridge between the five threefold-axis Rb^+ ions, and three bridge between the Rb^+ ions in the sodalite unit.

Under-coordinated, large monovalent cations were observed in the crystal structures of dehydrated Cs_7Na_5-A[1,2] and K_{12}-A[2,3], including a zero-coordinate K^+ ion in the latter structure. This work was undertaken primarily to reconfirm the existence of a zero-coordinate cation in a more ideal experimental situation. The previously reported exchange limit of Rb^+ ions for the 12 Na^+ ions per unit cell in zeolite A is 8.3[4] or 8.4.[5] It was hoped that a more intensive exchange procedure would lead to a completely exchanged (or nearly so) sample. If successful, it was anticipated that an uncoordinated Rb^+ ion would exist in the dehydrated Rb^+-exchanged structure. In dehydrated K_{12}-A,[3] the 12th K^+ ion was located deep in the large cavity, 4.25 Å from the nearest framework ion, an oxide ion of a 6-oxygen ring.[6] This distance is 1.6 Å greater than the sum of the corresponding ionic radii.[7] At such long distances, this K^+ ion could be considered uncoordinated.

Recent IR studies of hydrated Rb^+-exchanged zeolite A have indicated that the Rb^+ ions are loosely bound to the framework.[4] The hydrated structure was done to observe the structural arrangement responsible for these IR results and to verify the cation composition of the dehydrated material.

This work on dehydrated Rb^+-exchanged zeolite A[8] is judged to be considerably more precise and definitive than that involving dehydrated K_{12}-A[3] because (1) the scattering factor of Rb^+ for x rays is approximately twice that of K^+, and (2) almost twice as much diffraction data were gathered using a crystal 50% larger by volume.

Experimental Section

Crystals of zeolite 4A were prepared by a modification of Charnell's method,[9] including a second crystallization using seed crystals from the first synthesis. A single crystal 0.10 mm on an edge was lodged in a fine glass capillary. Ion exchange was then performed using flow methods; 0.1 M aqueous RbOH was allowed to flow past the crystal at a velocity of approximately 1.0 cm/s. This procedure was conducted at 25 (1) °C for 8 days. The crystal was then dehydrated for a period of 48 h at 350 °C and 1×10^{-5} Torr. After cooling to room temperature, the crystal in its capillary was removed from the vacuum line by torch. Its appearance was unaltered by these exchange and dehydration procedures.

The hydrated crystal (0.09 mm on an edge) used in this study was prepared by the same procedure, except that the flow exchange process lasted only 7 days. The hydrated crystal remained in its capillary during data collection. Subsequent diffraction intensities for both crystals were collected at 23 (1) °C.

Chemical analysis was not attempted, since only one crystal was exchanged in each case, and because least-squares refinement of the Rb^+ ions was expected to yield a definitive result. The zeolite has a unit cell composition of $Rb_{11}Na_1Si_{12}Al_{12}O_{48}$, exclusive of water molecules, and will be subsequently referred to as $Rb_{11}Na_1$-A.

The cubic space group $Pm3m$ (no systematic absences) appeared to be appropriate.[6a,10-13] A Syntex four-circle computer-controlled diffractometer with a graphite monochromator and a pulse-height analyzer was used throughout for preliminary experiments and for the collection of diffraction intensities. Molybdenum radiation ($K\alpha_1$, λ = 0.70930 Å; $K\alpha_2$, λ = 0.71359 Å) was used throughout. In each case, the cell constant, a = 12.261 (2) Å for the dehydrated crystal and a = 12.321 (3) Å for the hydrated crystal, was determined by a least-squares treatment of 15 intense reflections with $2\theta < 24°$.

The θ–2θ scan technique was employed at a constant scan rate of 1.0°/min (in 2θ). The scan range varied from 2.0° at 2θ = 3° to 2.5° at 2θ = 70°. One-half of the total scan time was spent counting background at each end of the scan range. All unique reciprocal lattice points (880 and 890 for the dehydrated and hydrated crystals, respectively) with $3° < 2\theta < 70°$ were examined. The high upper limit for 2θ was chosen to maximize the size of the data sets, even though few reflections with large 2θ values showed significant intensity. Three check reflections, monitored in each data collection after every 100 reflections, indicated no significant variation in intensity.

Standard deviations were assigned according to the formula:

$$\sigma(I) = [\omega^2\{CT + 0.25(t_c/t_b)^2(B_1 + B_2)\} + (pI)^2]^{1/2}$$

where ω is the scan rate, CT is the total integrated count obtained in a scan time t_c, B_1 and B_2 are the background counts each obtained in time t_b, and $I = \omega[CT - 0.5(t_c/t_b)(B_1 + B_2)]$. A value of 0.02 was assigned to the empirical parameter p to account for instrumental instability. The net counts were then corrected for Lorentz and polarization effects, including that of the monochromator crystal, which was assumed to be half perfect and half mosaic in character. An absorption correction (μ = 8.8 mm^{-1}) was applied to the dehydrated data set, but had no significant effect on the final structure.

Only those reflections in each data set for which the net counts exceeded three times the corresponding esd's were used in structure

Table I. Positional, Thermal,[a] and Occupancy Parameters for $Rb_{11}Na_1$-A

	Wyckoff position	x	y	z	β_{11} or B_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy factor
a. Dehydrated											
(Si,Al)	24(k)	0	1852 (2)	3753 (2)	21 (2)	20 (2)	14 (2)	0	0	7 (3)	1[b]
O(1)	12(h)	0	2405 (8)	½	43 (11)	49 (9)	23 (9)	0	0	0	1
O(2)	12(i)	0	2871 (6)	2871 (6)	44 (9)	36 (6)	36 (6)	0	0	22 (14)	1
O(3)	24(m)	1122 (4)	1122 (4)	3530 (6)	44 (4)	44 (4)	50 (7)	18 (11)	−1 (8)	−1 (8)	1
Rb(1)	8(g)	2514 (2)	2514 (2)	2514 (2)	58 (13)	58 (13)	58 (13)	37 (4)	37 (4)	37 (4)	⅝
Rb(2)	3(c)	0	½	½	116 (7)	125 (4)	125 (4)	0	0	0	1
Rb(3)	8(g)	3629 (47)	3629 (47)	3629 (47)	1127 (153)	1127 (153)	1127 (153)	−480 (251)	−480 (251)	−480 (251)	⅛
Rb(4)	8(g)	1125 (13)	1125 (13)	1125 (13)	73 (10)	73 (10)	73 (10)	17 (26)	17 (26)	17 (26)	⅛
Rb(5)	8(g)	1456 (12)	1456 (12)	1456 (12)	3.4 (6)						⅛
Na	8(g)	1904 (27)	1904 (27)	1904 (27)	−0.5 (7)						⅛
b. Hydrated											
(Si, Al)	24(k)	0	1827 (6)	3720 (5)	24 (6)	12 (6)	11 (5)	0	0	9 (9)	1[b]
O(1)	12(h)	0	2250 (2)	½	111 (4)	68 (3)	11 (2)	0	0	0	1
O(2)	12(i)	0	2896 (12)	2896 (12)	50 (22)	5 (11)	5 (11)	0	0	−33 (29)	1
O(3)	24(m)	1125 (11)	1125 (11)	3443 (15)	54 (12)	54 (12)	93 (21)	43 (29)	41 (25)	41 (25)	1
Rb(1)	8(g)	2667 (5)	2667 (5)	2667 (5)	87 (6)	87 (6)	87 (6)	101 (13)	101 (13)	101 (13)	⅝
Rb(2A)	3(c)	0	½	½	74 (47)	199 (44)	199 (44)	0	0	0	⅓
Rb(2B)	24(m)	941 (44)	4539 (32)	4539 (32)	12 (3)						1/12
Rb(3)	8(g)	1130 (22)	1130 (22)	1130 (22)	13 (1)						¼
Rb(4)	24(l)	2189 (81)	3412 (74)	½	5 (2)						1/24
O(4)	12(j)	2689 (61)	2689 (61)	½	6 (3)						⅓
O(5)	12(i)	0	902 (58)	902 (58)	7 (5)						¼

[a] Positional and anisotropic thermal parameters are given ×10^4; isotropic thermal parameters are in Å^2. Numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding parameter. See Figures 1 and 4 for the identities of the atoms. The anisotropic temperature factor = $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] Occupancy for (Si) = ½; occupancy for (Al) = ½.

solution and refinement. This amounted to 300 unique reflections for the dehydrated crystal and 226 for hydrated $Rb_{11}Na$-A, relatively large numbers considering the high symmetry of the group.

Structure Determination

Dehydrated $Rb_{11}Na_1$-A. Full-matrix least-squares refinement of dehydrated $Rb_{11}Na_1$-A began using the principal exchangeable cation coordinates (adjusted to account for the differing ionic radii) and framework positions of dehydrated K_{12}-A.[3] Anisotropic refinement of the framework atoms and isotropic refinement of the Rb^+ positions were used for this initial model, which consisted of eight Rb(1)'s and three Rb(2)'s as the exchangeable cations. Refinement converged to an R_1 index, $(\sum|F_o - |F_c||)/\sum F_o$, of 0.287 and an R_2 weighted index, $(\sum w(F_o - |F_c|)^2/\sum wF_o^2)^{1/2}$ of 0.271. A subsequent difference Fourier function revealed a peak of approximately 3.9 e Å^{-3} at (0.36, 0.36, 0.36) and also a very elongated area of electron density averaging approximately 8.0 e Å^{-3} ranging from (0.11, 0.11, 0.11) to (0.16, 0.16, 0.16). This latter peak was easily resolved into two nonequivalent Rb^+ ions (Rb(4) and Rb(5)) in the sodalite unit. The peak at (0.36, 0.36, 0.36), corresponding to the expected position for an uncoordinated Rb^+ ion, Rb(3), was stable in least-squares refinement. The occupancies of Rb(1) and Rb(2) refined well to a definitive result of five and three ions per unit cell, respectively. This is in contrast to the six K(1)'s in dehydrated K_{12}-A.[3] Anisotropic refinement of the framework and Rb^+ positions, except for Rb(5) and Na^+, which were treated isotropically, converged with the error indices $R_1 = 0.087$ and $R_2 = 0.055$.

A trial removal of Rb(3) from least-squares refinement resulted in an R_2 index of 0.063, a significant increase. An attempt was made to refine an alternative structure based on ten Rb^+ ions (Rb(3) absent) and two Na^+ ions. Least-squares refinement based on this model resulted in unstable refinement of the Na^+ ions with a very large isotropic temperature parameter. The R_2 index for this model was 0.085.

The goodness-of-fit, $(\sum w(F_o - |F_c|)^2/(m - s))^{1/2}$, is 2.90; m (300) is the number of observations, and s (35) is the number of variables in least squares. All shifts in the final cycle of least-squares refinement were less than 1% of their corresponding esd's. The final structural parameters are presented in Table Ia. Interatomic distances and angles are given in Table IIa. A listing of the observed and calculated structure factors is available in the microfilm edition; see the paragraph at the end of this paper regarding supplementary material. The structure is shown in Figure 1.

For dehydrated $Rb_{11}Na_1$-A, the largest peak on the final difference Fourier function, whose estimated standard deviation is 0.12 e Å^{-3}, was 2.9 e Å^{-3} in height. This peak was unusually narrow and was located at (0.25, 0.25, 0.25), the Rb(1) position.

Hydrated $Rb_{11}Na_1$-A. Using the framework and K(1) parameters of hydrated K_{12}-A,[3] initial full-matrix least-squares refinement of hydrated $Rb_{11}Na_1$-A converged to R_1 and R_2 indices of 0.30 and 0.29, respectively. Successive difference Fourier syntheses and least-squares refinements served to reveal the positions of 11 Rb^+ ions and seven water molecules. The Rb^+ ions are distributed among five equipoints, five at (0.26, 0.26, 0.26), two at (0.09, 0.45, 0.45), two at (0.11, 0.11, 0.11), one at (0, 0.5, 0.5), and one at (0.22, 0.34, 0.5). The water molecules are distributed among two equipoints, four at (0.27, 0.27, 0.5) and three at (0, 0.09, 0.09).

The final values of R_1 and R_2 are 0.134 and 0.100, and the goodness-of-fit is 4.6. The large error indices suggest that some water molecules, presumably at positions of low occupancy, were not located. Specifically, water molecules associated with Rb(2A), Rb(2B), and Rb(4) were not found.

All shifts in the final cycle of refinement were less than 1% of their corresponding esd's. The final structural parameters

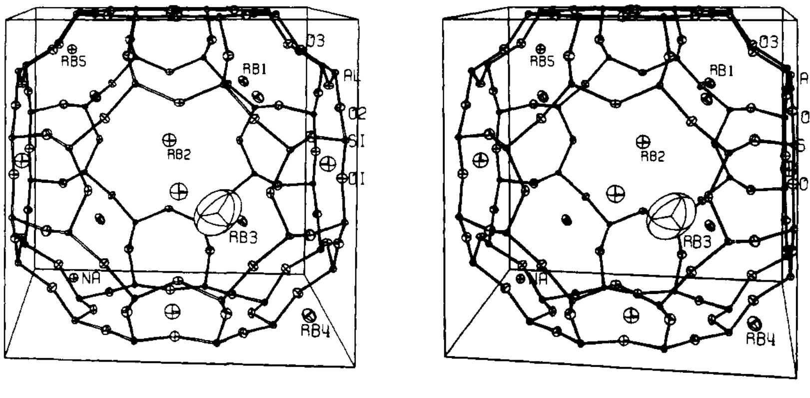

Figure 1. Stereoview[14] of dehydrated $Rb_{11}Na_1$-A. Ellipsoids of 20% probability are shown. The thermal parameter of Na was increased by 3.5 σ for the purposes of the drawing.

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

	a. Dehydrated $Rb_{11}Na_1$-A		
(Si,Al)-O(1)	1.673 (5)	O(1)-(Si,Al)-O(2)	106.9 (5)
(Si,Al)-O(2)	1.652 (3)	O(1)-(Si,Al)-O(3)	111.6 (4)
(Si,Al)-O(3)	1.664 (2)	O(2)-(Si,Al)-O(3)	107.4 (4)
		O(3)-(Si,Al)-O(3)	111.6 (5)
Rb(1)-O(3)	2.716 (7)	(Si,Al)-O(1)-(Si,Al)	132.2 (6)
Rb(1)-O(2)	3.144 (3)	(Si,Al)-O(2)-(Si,Al)	171.8 (7)
Rb(2)-O(1)	3.181 (10)	(Si,Al)-O(3)-(Si,Al)	149.6 (3)
Rb(2)-O(2)	3.692 (7)		
Rb(3)-O(1)	4.98 (5)	O(3)-Rb(1)-O(3)	100.5 (3)
Rb(3)-O(2)	4.64 (8)	O(3)-Rb(3)-O(3)	57.4 (9)
Rb(3)-O(3)	4.35 (8)	O(3)-Rb(4)-O(3)	90.2 (5)
Rb(4)-O(3)	2.949 (17)	O(3)-Rb(5)-O(3)	106.4 (3)
Rb(5)-O(3)	2.608 (12)	O(3)-Na-O(3)	119.9 (6)
Na-O(2)	2.874 (6)		
Na-O(3)	2.411 (7)		
Rb(3)-Rb(1)	5.11 (2)		
Rb(3)-Rb(2)	5.045 (12)		
Rb(3)-Rb(4)	5.32 (10)		
Rb(3)-Na	6.240 (13)		
	b. Hydrated $Rb_{11}Na_1$-A		
(Si,Al)-O(1)	1.661 (11)	O(1)-(Si,Al)-O(2)	109.3 (12)
(Si,Al)-O(2)	1.663 (8)	O(1)-(Si,Al)-O(3)	110.9 (7)
(Si,Al)-O(3)	1.669 (5)	O(2)-(Si,Al)-O(3)	106.6 (9)
		O(3)-(Si,Al)-O(3)	112.3 (14)
Rb(1)-O(3)	2.851 (18)	(Si,Al)-O(1)-(Si,Al)	143.4 (18)
Rb(1)-O(4)	2.875 (2)	(Si,Al)-O(2)-(Si,Al)	165.2 (15)
Rb(2A)-O(1)	3.39 (3)	(Si,Al)-O(3)-(Si,Al)	144.9 (13)
Rb(2A)-O(2)	3.66 (2)		
Rb(2B)-O(1)	3.10 (4)	O(3)-Rb(1)-O(3)	90.2 (6)
Rb(2B)-O(2)	3.09 (6)	O(4)-Rb(1)-O(4)	88.9 (29)
Rb(3)-O(3)	2.85 (3)	O(2)-Rb(1)-O(2)	99.3 (7)
Rb(3)-O(5)	2.88 (7)	Rb(1)-O(4)-Rb(1)	178.4 (25)
Rb(1)-O(2)	3.310 (3)	O(1)-Rb(2B)-O(1)	101.1 (15)
Rb(3)-O(2)	3.38 (3)	O(2)-Rb(2B)-O(2)	94.5 (10)
O(5)-O(5)	2.72 (17)	O(1)-Rb(2B)-O(2)	43.4 (7)
O(5)-O(3)	4.24 (2)	O(3)-Rb(3)-O(3)	90.2 (16)
Rb(3)-Rb(3)	4.82 (59)	O(2)-Rb(3)-O(2)	96.6 (12)
Rb(4)-O(1)	3.05 (10)	O(5)-Rb(3)-O(5)	56.4 (12)
		Rb(3)-O(5)-Rb(3)	113.8 (33)

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

Table III. Deviations of Atoms (Å) from Planes[a]

(a) From the (111) Plane at O(3)

Dehydrated $Rb_{11}Na_1$-A		Hydrated $Rb_{11}Na_1$-A	
Rb(1)	1.25	Rb(1)	1.64
Rb(3)	3.62	Rb(3)	−1.64
Rb(4)	−1.70	O(4)	3.33
Rb(5)	−0.99	O(5)	−4.05
Na	−0.04		

(b) From the (111) Plane at Rb(2)

Dehydrated $Rb_{11}Na_1$-A	
O(1)[b]	−1.84
O(2)[b]	−3.01
O(3)[b]	−2.99
Rb(1)	1.78
Rb(3)[b]	0.63
Na	1.35

[a] A negative deviation indicates that the atom lies on the same side of the plane as the origin. [b] These four ions are associated with the same threefold axis.

are presented in Table Ib. Interatomic distances and angles are given in Table IIb. See the paragraph at end of this paper regarding supplementary material.

The full-matrix least-squares program used[14] in all structure determinations minimized $\sum w(\Delta|F|)^2$; the weights (w) were the reciprocal squares of σ, the standard deviation of each observation. Atomic scattering factors[15] for Rb^+, 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. The scattering factors for Rb^+ and $(Si,Al)^{1.75+}$ were modified to account for the real component ($\Delta f'$) of the anomalous dispersion correction.[16]

Discussion

In the dehydrated structure (see Tables Ia, IIa, and III, and Figures 1, 2, and 3), 8 of the 11 Rb^+ ions per unit cell are distributed over four nonequivalent threefold axis equipoints, while the remaining three lie at the centers of the 8-oxygen rings. The Rb(1) ions, of which there are five, are located in the large cavity, 1.25 Å from the O(3) plane of the oxygen 6-rings. Two nonequivalent Rb^+ ions, Rb(4) and Rb(5), are located inside the sodalite unit near the 6-rings, 1.69 and 0.99 Å, respectively, from the [111] plane at O(3). Rb(1), Rb(4), and Rb(5) are trigonally coordinated to their respective sets of three framework O(3)'s at 2.716, 2.949, and 2.608 Å.

The uncoordinated ion, Rb(3), is located deep within the large cavity, 3.62 Å from the O(3) plane. Its closest approach to a framework atom (to three O(3)'s of an empty 6-ring) is 4.35 (8) Å, which is 1.56 Å greater than the sum of the corresponding ionic radii. The large Rb(3) thermal ellipsoid (see Figures 2 and 3) is very much like that of K(3), the uncoordinated K^+ ion in dehydrated K_{12}-A,[3] in its magnitude and orientation, and is consistent with its environment.

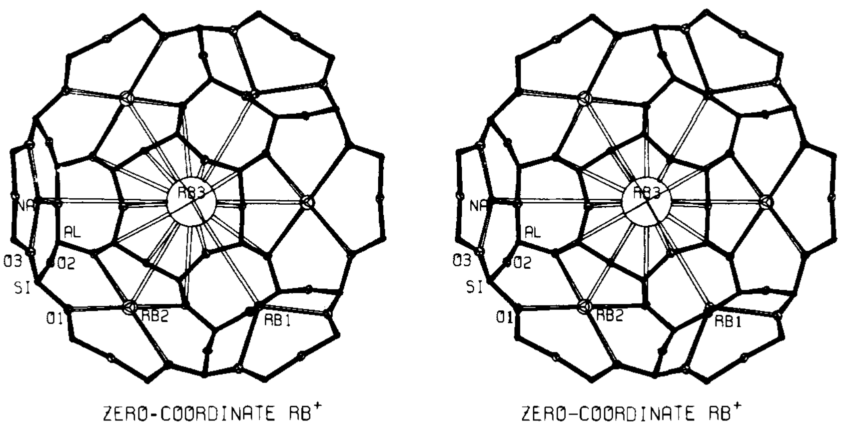

Figure 2. A stereoview,[14] approximately along the threefold axis, of half of the large cage, showing all Rb(3)-O distances less than 5.0 Å and all Rb(3)-Rb distances less than 5.3 Å. The Rb(4) ion, which is 5.31 Å from Rb(3), along the direction of view is not shown. Other comments in the caption to Figure 1 apply here as well.

The crystal studied was dehydrated; the unusual Rb(3) position cannot be attributed to residual water molecules. The dehydration conditions employed were more than sufficient to remove all water from Na^+,[6a] K^+,[3] Co(II),[17] and Mn(II),[18] and Rb^+ is more labile toward water exchange than any of those. If Rb(3) were occupied by a water oxygen instead of Rb^+, the hydration distance to Rb(1) would be 2.37 Å, far from the acceptable 2.88 Å distance observed in the subsequently determined structure of hydrated $Rb_{11}Na_1$-A. The 11 Rb^+ ions located in that structure must remain present after dehydration, and one Rb^+ cannot be placed elsewhere than at Rb(3).

The position of Rb(3) cannot be governed by electrostatics alone since, according to the Laplace equation $\nabla^2 V = 0$, as applied here, there is no electrostatic minimum inside the large cage for Rb(3) to occupy. Apparently, the usual chemical attractive and repulsive forces have balanced to give a shallow energy minimum at an unusual position. Even though Rb(3) is in a somewhat asymmetric environment due to the Na^+ ion, it should remain on the threefold axis because of its attraction to framework oxygens and its repulsion from three Rb(2)'s. Figures 2 and 3 show Rb(3) in relation to its nearest neighbors, which are either members of the nearest 6-ring or are arranged symmetrically about that ring. They are three O(3)'s at 4.35 Å, three O(2)'s at 4.64 Å, six O(1)'s at 4.98 Å, three Rb(2)'s at 5.04 Å, two Rb(1)'s at 5.11 Å, and a single Rb(4) at 5.32 Å.

As in dehydrated K_{12}-A,[3] it is necessary that Rb(3), Rb(4), and Rb(5) be on the same threefold axis to minimize Rb^+-Rb^+ repulsions. This leaves five Rb(1)'s and one Na^+ ion to occupy the six remaining 6-rings per unit cell. The Na^+ ion has been placed in one of the three 6-rings nearest Rb(3) to minimize repulsions. Also, the two Rb^+ ions in the sodalite unit, Rb(4) and Rb(5), must be on opposite sides of the sodalite unit, and Rb(3) and Rb(4) must be on opposite sides of the same 6-ring. By this model, the intercationic distances are as large as possible: Rb(3)-Rb(4), 5.32 Å, and Rb(4)-Rb(5), 5.48 Å. The fact that there are two nonequivalent Rb^+ ions in the sodalite unit is in itself strong evidence for the existence of one Rb^+ ion at Rb(3). If Rb(3) were not present, then Rb(4) and Rb(5) would be the only Rb^+ ions on that particular threefold axis, and thus would be expected to be equivalent.

The three Rb(2) ions are located at the centers of the 8-oxygen rings, filling that equipoint, at sites of D_{4h} symmetry, 3.18 Å from four O(1)'s and 3.69 Å from four O(2)'s. The Rb(1)-O(1) distance is long by 0.4 Å as compared to the sum of the appropriate radii,[7] indicating that these Rb^+ ions are "loosely bound" as was observed spectroscopically for the hydrated zeolite by Maxwell and Baks.[4] The same situation was observed crystallographically in dehydrated Cs_7Na_5-A.[1]

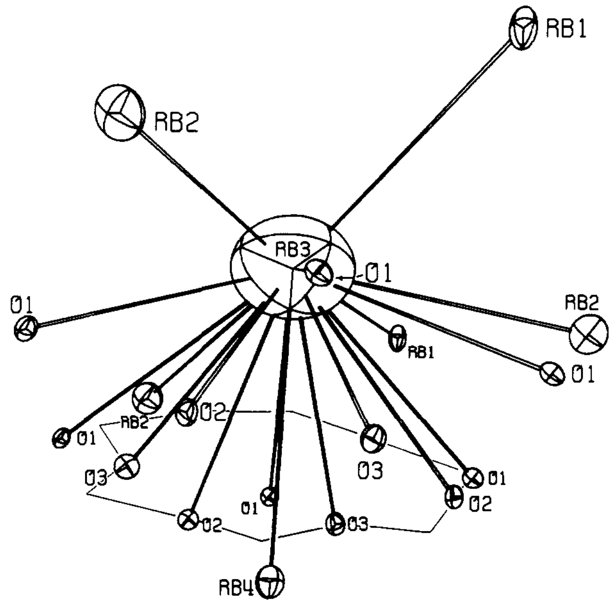

Figure 3. The 18 nearest neighbors of the zero-coordinate cation, Rb(3), are shown using ellipsoids of 20% probability. The oxygen 6-ring closest to Rb(3) is indicated.

An alternative interpretation, also very unusual, of these structural results was considered, namely that a neutral Rb atom occupies the Rb(3) site. The radius of Rb is approximately 1.0 Å greater than that of Rb^+,[19] and would be more consistent with the long approach distances observed. The neutral Rb atom could conceivably have formed by the extremely unfavorable reaction $2Rb^+ + 2H_2O \rightarrow 2Rb + 2H^+ + H_2O_2$, which might have proceeded to the right because of the ability of the small H^+ ions to approach the zeolite framework at conventional distances, and because any H_2O_2 that might have formed would have been removed from the equilibrium by the vacuum system. The hypothesis was rejected by the direct observation of the rehydration of the very same crystal used in the diffraction experiments. Upon being exposed to water, and while covered by water and in view under a microscope, no gas was produced by the expected raction $2Rb + 2H_2O \rightarrow 2RbOH + H_2$. Furthermore, at no time during the entire history of the crystal did it darken, as would be expected if rubidium atoms formed and clustered into large particles.

Hydration leaves the positions of the framework atoms almost unchanged, but those of the cations are modified (see

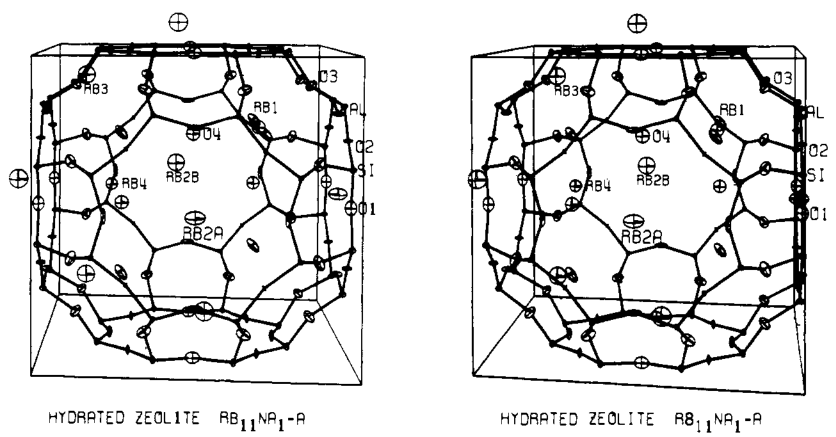

Figure 4. A stereoview[14] of the large cavity of hydrated $Rb_{11}Na_1$-A using ellipsoids of 20% probability. The β_{23} thermal parameter on O(2) was increased by 1.5 σ to produce a positive-definite thermal ellipsoid.

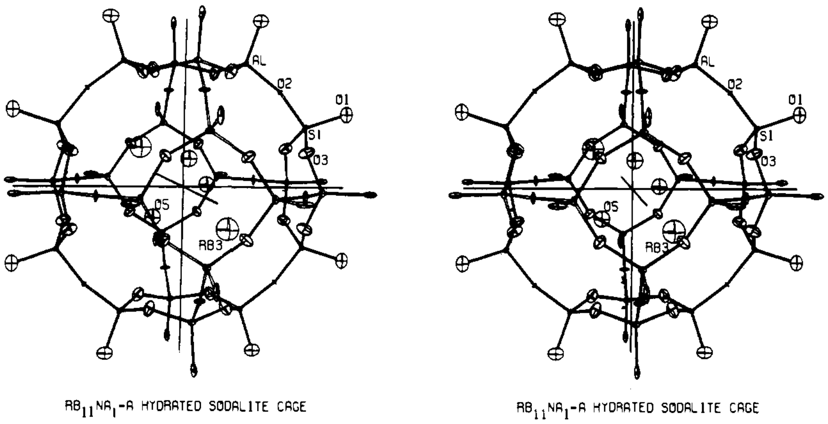

Figure 5. A stereoview[14] of the sodalite cavity of hydrated $Rb_{11}Na_1$-A. Other comments in the caption to Figure 4 apply here as well.

Tables Ib, IIb, and III, and Figures 4 and 5). The two Rb^+ ions in the sodalite unit become equivalent, occupying position Rb(3) (not to be confused with position Rb(3) in dehydrated $Rb_{11}Na_1$-A). Three water molecules arranged trigonally about the origin bridge between the Rb(3)'s in hydrated $Rb_{11}Na$-A (see Figure 5). This is in contrast to hydrated K_{12}-A,[3] where only water molecules occupy the sodalite unit. Five Rb(1)'s remain opposite the 6-rings in the large cavity, but the Rb(1)-O(3) distance has increased by 0.13 Å. An O(4) water molecule bridges between each Rb(1) position, to give a total of four O(4)'s per unit cell. This kind of bridging was also found in hydrated K_{12}-A.[3]

A single ion at Rb(4), a position in the large cavity, shows a closest framework approach of 3.05 Å to an O(1) atom. The water molecules which might be expected to associate with this ion were not located.

Upon hydration, two of the three Rb^+ ions associated with the 8-ring shift off the plane at (0, 0.5, 0.5) to the position Rb(2B). The Rb(2B)'s are also only loosely bound to the framework: Rb(2B)-O(1), 3.10 Å; and Rb(2B)-O(2), 3.09 Å. Presumably, they have been shifted off the plane of the 8-ring by an asymmetric interaction with unlocated water molecules. The remaining Rb^+ ion, Rb(2A), associated with the 8-ring, remains at (0, 0.5, 0.5), far from its nearest framework oxygen. Rb(2A)'s coordination sphere of water molecules also could not be located. The Na^+ ion, probably occupying a 6-ring as in dehydrated $Rb_{11}Na_1$-A, could not be located in the hydrated structure. Anisotropic refinement of all Rb^+ ions and water molecules was attempted, but this model was unstable in least squares. This is presumably ascribable to unlocated water molecules. In hydrated $Rb_{11}Na_1$-A, Rb(2A), Rb(2B), and Rb(4) are "loosely bound", judging by their distances to framework ions; it is these positions, apparently, which account for the IR results.[4]

The existence of zero-coordinate cations, such as those found in dehydrated K_{12}-A[3] and now in dehydrated $Rb_{11}Na_1$-A are governed by certain conditions which must be met by the zeolite and by the cations. First, it is essential that the zeolite have a high Al/Si ratio to maximize the anionic charge density of its framework. This ratio is 1.0 in zeolite A, its maximum value according to Loewenstein's rule.[20] Secondly, large monovalent cations are required which "coat" the inner surface of the zeolite, filling all possible coordination sites before all negative charges of the framework have been balanced. In dehydrated K_{12}-A[3] and dehydrated $Rb_{11}Na_1$-A, the 12th negative charge per unit cell is balanced by a cation for which no framework coordination site remains available, a situation analogous to the dilemma in "musical chairs", a children's game. In the structure of dehydrated Na_{12}-A,[6a] the 12th Na^+ ion occupies a coordination site opposite a 4-oxygen ring; this site is unavailable to the larger monovalent cations K^+ and Rb^+. It is further necessary that the +1 oxidation state be quite stable, as it is for potassium and rubidium, so that reduction to the metal cannot occur by a mechanism such as the one previously mentioned.

In dehydrated $Rb_{11}Na_1$-A, it is a Rb^+ ion which is uncoordinated, not the Na^+ ion, because the latter can make a closer and more favorable approach to the oxygens of a 6-ring.

These results allow us to employ a stringent definition of noncoordination. If the distance between two ions exceeds the sum of their corresponding radii by more than 1.0 Å, then these ions may be considered not bonded or uncoordinated. At least, their bond order is much less than one. On this basis, Rb(3) in dehydrated $Rb_{11}Na_1$-A is termed zero-coordinate, zero being the sum of integers, all zero, describing its bond orders to its nearest neighbors. For this structure, the rounded-off value of 1.0 Å used in the criterion stated above may be raised to 1.5 Å.

Acknowledgment. This work was supported by the National Science Foundation (Grant No. MPS73-08761). We are indebted to the University of Hawaii Computing Center.

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

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Chemical–Structural Properties of Tetracycline Derivatives. 3. The Integrity of the Conformation of the Nonionized Free Base[1]

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Abstract: A second crystal structure modification of anhydrous oxytetracycline free base, OXY, has been obtained by slow evaporation of a warm, water free toluene solution. A crystal structure analysis has been carried out with intensity data measured from a cooled crystal (*ca.* −150 °C). The crystal displays space group symmetry $P2_12_12_1$ with one molecule per asymmetric unit and lattice parameters: $a = 8.836$ (1), $b = 12.416$ (1), and $c = 18.760$ (2) Å. The crystal was found to consist of fully associated (nonzwitterionic) OXY molecules displaying the same conformation observed in the first modification, but differences in inter- and intramolecular hydrogen bonding are observed. A reinterpretation of reported proton NMR data[12,14] confirms the proposal[2] that the tetracycline derivatives are likely to be nonzwitterionic in nonaqueous solvents. Some consequences of the misconception that the free base derivatives are zwitterionic in Me_2SO, particularly with respect to metal bonding, are discussed.

Crystal structure analyses have been reported for two forms of oxytetracycline, OXY, free base,[2] a dihydrate and an anhydrous form. The structure analyses have demonstrated that the molecular moieties in the crystals differ both in chemical structure and in conformation. The dihydrate crystals consist of zwitterionic microspecies in which the dimethylamine group at C(4) is protonated, while the negative charge is distributed over the A ring chromophore in a manner correlatable with the orientation of the amide substituent at C(2). The anhydrous crystals were found to contain nonionized molecular moieties with a clearly enolic A ring chromophore. Conformationally, the zwitterion was found to be very similar to the several examples that have been reported for the fully protonated cationic derivatives,[3,4] while the nonionized molecule displayed the conformation initially proposed by Schach von Wittenau and Blackwood[5] from NMR studies and subsequently observed for crystalline 5,12a-diacetyloxytetracycline.[6] The report presenting these structures[2] raised the possibility that both modifications of the free base might be important to the biological activity of the broad spectrum tetracycline antibiotics. While the zwitterionic form is quite likely adopted in aqueous rich regions of the body, it was felt that the nonionized form presented a more suitable model for the more hydrophobic regions.

A second crystal modification of anhydrous oxytetracycline, OXY(II), had been crystallized under very similar conditions to those which produced the first modification, OXY(I).[2] Its crystal structure analysis was undertaken to determine whether or not the free base had adopted an alternative conformation and/or chemical structure, a distinct possibility in view of the possible A ring tautomerism.[3a,7]

Experimental Section

Anhydrous OXY free base was dissolved in warm (~70 °C) water-free toluene and maintained on a hot plate at approximately this temperature to allow slow evaporation, with refluxing, of the solvent. Crystals, displaying rectangular prismatic morphology rather