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34. A table including all calculated vibrational frequencies of BP in the triplet state can be available upon the request to the author.

Crystal Structure of Dehydrated Rb⁺-Exchanged Zeolite X, $Rb_{71}Na_{21}Si_{100}Al_{92}O_{384}$

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The crystal structure of dehydrated Rb⁺-exchanged zeolite X, stoichiometry $Rb_{71}Na_{21}$-X ($Rb_{71}Na_{21}Si_{100}Al_{92}O_{384}$) per unit cell, has been determined from single-crystal X-ray diffraction data gathered by counter methods. The structure was solved and refined in the cubic space group $Fd3$, $a=25.007(3)$ Å at 21(1) °C. The crystal was prepared by ion exchange in a flowing stream using a 0.05 M aqueous RbOH solution (pH=12.7). The crystal was then dehydrated at 360 °C and 2×10^{-6} torr for two days. The structure was refined to the final error indices, $R_1=0.047$ and $R_2=0.040$ with 239 reflections for which $I > 3\sigma(I)$. In this structure, 71 Rb⁺ ions per unit cell are found at six different crystallographic sites and 21 Na⁺ ions per unit cell are found at two different crystallographic sites. Four and a half Rb⁺ ions are located at site I, the center of the hexagonal prism. Nine Rb⁺ ions are found at site I' in the sodalite cavity (Rb-O=2.910(15) Å and O-Rb-O=78.1(4)°). Eighteen Rb⁺ ions are found at site II in the supercage (Rb-O=2.789(9) Å and O-Rb-O=92.1(4)°). Two and a half Rb⁺ ions, which lie at site II', are recessed ca. 2.07 Å into the sodalite cavity from their three O(2) oxygen planes (Rb-O= 3.105(37) Å and O-Rb-O=80.6(5)°). Thirty-two Rb⁺ ions are found at site III deep in the supercage (Rb-O= 2.918(12) Å and O-Rb-O=71.9(4)°), and five Rb⁺ ions are found at site III'. Seven Na⁺ ions also lie at site I. Fourteen Na⁺ ions are found at site II in the supercage (Na-O=2.350(19) Å and O-Na-O=117.5(6)°).

Introduction

Many structural investigations have been devoted to the characterizations of cation distributions in faujasite-type zeolites. Most of these studies have been summarized by Mortier.[1] Alkali-metal cations other than sodium ions are of interest for use in catalysis and sorption. The crystal structure of hydrated sodium zeolite X was determined by Broussard and Shoemaker[2] using powder X-ray diffraction techniques. It was reinvestigated by Olson using single-crystal X-ray diffraction techniques.[3]

Recently, only a few studies of dehydrated group I cation exchanged zeolite X have been done.[4-6] The structures of dehydrated Na_{88}-X[4], fully dehydrated K^+-exchanged zeolite X, K_{92}-X[5], and Tl^+-exchanged zeolite X, Tl_{92}-X[6], were determined. In the structure of Na_{88}-X,[4] all eighty-eight Na^+ ions were located at seven crystallographically non-equivalent sites (a large number) as described in Table 1. In the structure of dehydrated K^+-exchanged zeolite X,[5] about 88 (insignificantly less than all 92) K^+ ions were located at four sites as described in Table 1. Takaishi has proposed a comprehensive explanation of the cation distribution in Na_{88}-X[4] based Si/Al ordering.[7,8] In the structure of Tl_{92}-X,[6] Tl^+ ions are found at four different crystallographic sites, no Tl^+ ions occupy site I; they remain empty. Smolin et al.[9] successfully synthesized and determined dehydrated partially K-, Cs-exchanged zeolite X, but dehydrated partially Rb^+-exchanged zeolite X crystal was destroyed and could not determined its structure.

This work was initiated to investigate the cation positions in the crystal structure of the dehydrated fully Rb^+-exchanged zeolite X. If fully Rb^+-exchanged zeolite X could not be obtained, the structural basis of limit would be seen and the site selectivities for two ions (Rb^+ and Na^+ ion) of different ionic radii would be learned.

Experimental Section

Large single crystal of sodium zeolite X, stoichiometry $Na_{92}Si_{100}Al_{92}O_{384}$, were prepared in St. Petersburg, Russia.[10] One of these, a colorless octahedron about 0.25 mm in cross-section was lodged in a fine Pyrex capillary. Ion exchange was performed by the flow method: 0.05 M aqueous RbOH solution (Aldrich, 99.9%) was allowed to flow past the crystal at a velocity of approximately 0.5 cm/s for 3 days at 25 °C. Then the crystal was dehydrated at 360 °C and 2×10^{-6} torr for 48 h. The resulting colorless crystal was sealed off, under vacuum in its capillary, from the reaction vessel by torch after cooling to 25 °C.

The space group $Fd\overline{3}$ was used throughout this work.[11] This choice is supported by (a) the low Si/Al ratio which in turn requires, at least in short range, alteration of Si and Al and (b) the observation that this crystal, like all other crystals from the same batch, does not have intensity symmetry across (110) and therefore lacks that mirror plane. Diffraction data were collected with an automated Enraf-Nonius four-circle computer-controlled CAD-4 diffractometer equipped with a pulse-height analyzer and a graphite monochromator, using Mo Kα radiation ($K\alpha_1$, λ= 0.70930 Å, $K\alpha_2$, λ=0.71359 Å). The unit cell constant at 21(1) °C determined by least-squares refinement of 25 intense reflections for which $14° < 2\theta < 24°$ is a=25.007(3) Å.

The ω-2θ scan technique was used. The data were collected using variable scan speeds. Most reflections were observed at slow scan speeds, ranging between 0.24 and 0.34 deg min^{-1} in ω. The intensities of three reflections in diverse regions of reciprocal space were recorded every 3h to monitor crystal and instrument stability. Only small random fluctuations of these check reflections were noted during the course of data collection. All unique reflections in the positive octant of an F-centered unit cell of which $2\theta < 50°$, $l > h$ and $k > h$ were examined by counter methods.

The raw data were corrected for Lorentz and polarization effects including incident beam monochromatization, and the resultant estimated standard deviations were assigned to each reflection by the computer programs GENESIS and BEGIN.[12] Of the 1407 unique reflections measured for Na_{21}-Rb_{71}-X, only the 239 reflections for which $I > 3\sigma(I)$ were used in subsequent structure determinations.

Structure Determination

Full-matrix least-squares refinement was initiated with the atomic parameters of the framework atoms [Si, Al, O(1), O(2), O(3), and O(4)] of Tl_{92}-X[6]. This model converged with an R_1 index, $\Sigma(|F_o - |F_c||)/\Sigma F_o$, of 0.38 and a weighted R_2 index, $(\Sigma w(F_o - |F_c|)^2/\Sigma wF_o^2)^{1/2}$, of 0.41.

A difference Fourier function revealed two large peaks at (0.125, 0.125, 0.4139) and (0.0, 0.0, 0.0) with heights of 6.9 and 6.2 eÅ^{-3}, respectively. Isotropic refinement including these as Rb^+ ions at Rb(5) and Na^+ ions at Na(1) converged to R_1=0.25 and R_2=0.27. The occupancy at Na(1) refined to 25.0(2). This is a 16-fold position and indicates that some Rb^+ ions also occupy at this side. A subsequent difference Fourier synthesis revealed a peak at Rb(4), (0.25, 0.25, 0.25) of height 8.1 eÅ^{-3}. Isotropic refinement of the framework atoms, Rb(5), Na(1), and Rb(4) (see Table 2) converged to R_1=0.16 and R_2=0.18.

A subsequent difference Fourier synthesis showed a peak at Rb(2), (0.080, 0.080, 0.080), with peak height 6.0 eÅ^{-3} and a peak at Na(2), (0.227, 0.227, 0.227), with peak height 2.2 eÅ^{-3}. Simultaneous refinement of positional and isotropic thermal parameters for the framework atoms, Na^+ ions at Na(1) and Na(2), and Rb^+ ions at Rb(2), converged to the error indices R_1=0.094 and R_2=0.090.

It is not difficult to distinguish Na^+ from Rb^+ ions for several reasons. Firstly, their atomic scattering factors are quite different, 10 e$^-$ for Na^+ vs 36 e$^-$ for Rb^+. Secondly, their ionic radii are different, Na^+=0.95 Å and Rb^+=1.48 Å.[13] Finally, the requirement that the cationic charges sum to +92 per unit cell does not allow the major positions to refine to acceptable occupancies with an alternative assignment of ionic identities.

The Rb^+ ion at site I' (Rb(2)) is only 3.48(1) Å from site I. By the low occupancy at site I', it appears that this short intercation distance should be avoided. If a D6R has either Na^+ or Rb^+ in it, then two adjacent sites I' are unoccupied. If a D6R does not contain any cation, then two Rb^+ ions lie outside at I' sites. The occupancy number at Rb(2) was refined to ca. 9.0. The occupancy at site I Na^+ ions was refined to 25.0(2) Na^+ ion, although the number of ions at this position can not be exceeded 11.5 (16.0-9/2=11.5) (for Na-X, K-X, Tl-X, and the most of divalent cation exchanged zeolite X,

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Table 1. Distribution of cations over sites

Site	I	I'	II	II'	III	III'
Maximum occupancy[a]	16	32	32	32	48	96[b]
Na$_{88}$-X[c]	2.9(5)	21.1(19), 8.0(19)	31.0(3)			10.6(10), 10.6(10), 8.6(10)
K$_{92}$-Xd	15.3(5)	12.5(8)	29.1(7)		21.2(10)	8.6(18)
Rb$_{71}$Na$_{21}$-X[e]	4.5(2)Rb$^+$, 7.0(2)Na$^+$	8.9(2)Rb$^+$	17.7(2)Rb$^+$, 12.7(7)Na$^+$	2.6(2)Rb$^+$	32.9(3)Rb$^+$	5.2(3)Rb$^+$
Tl$_{92}$-X[f]		31.8(4)	32.1(4)			16.3(5), 10.6(6)
Mg$_{46}$-X[g]	14.7(7)	4.2(11)	28.2(11)			
Ca$_{46}$-X[g]	16.3(5)		31.3(7)			
Ba$_{46}$-X[g]	13.6(1)	1.6(2)	28.9(2)			
Cd$_{46}$-X[h]	16.6(2)		29.5(2)			
Cd$_{24.5}$Tl$_{43}$-X[h]	14.6(7) Cd^{2+}		10.8(9)Cd^{2+}, 21.1(4)Tl$^+$		18.1(4) Tl$^+$	

[a]Ions per unit cell. [b]Due to crowding, all 96 sites may not be available. [c]Ref. 4. [d]Ref. 5. [e]Ref. This work. [f]Ref. 6. [g]Ref. 23. [h]Ref. 20.

cationic sites of I and I' are fully filled; $I + \dfrac{I'}{2} = 16$ (see Table 1)). Considering the relative scattering power of Na$^+$ and Rb$^+$, this indicates that some Rb$^+$ ions occupy this positions. So they are refined with identical positional parameters with the constraint in least-squares that the total number be 11.5. The occupancy numbers at Rb(1), Rb(2) and Na(1) refined to 4.5(2), 8.9(2), and 7.0(2), respectively.

A subsequent difference Fourier synthesis revealed two peaks at Rb(3), (0.167, 0.167, 0.167), with peak height 1.6 eÅ^{-3} and Rb(6), (0.042, 0.060, 0.442) with peak height 1.3 eÅ^{-3}. These peaks were stable in least-squares refinement.

Simultaneous refinement of positional and isotropic thermal parameters with varied occupancy numbers converged to the error indices R$_1$=0.079 and R$_2$=0.068. Anisotropic refinement of the framework atoms, Rb(1), Rb(2), Rb(3), Rb(4), Rb(5) and Na(1), and isotropic refinement of Rb(6) and Na(2), converged to R$_1$=0.047 and R$_2$=0.040 (see Table 1).

The intercation distance between Rb(4) and Na(2) at the same threefold axis is 1.17(1) Å. This is too close for ion to ion distance. Therefore these cations must occupy different threefold axes. The sum of the occupancy numbers at Rb(4)

and Na(2) was fixed at 32.0, the maximum value at these sites. The occupancy numbers at Rb(1), Rb(2), Rb(3), Rb(4), Rb(5), Rb(6), Na(1) and Rb(6) were fixed as shown in Table 1. The final error indices converged to R$_1$=0.047 and R$_2$= 0.040. The final difference Fourier function was featureless.

Atomic scattering factors for Si, Al, O , Rb$^+$ and Na$^+$ were used.[14,15] All scattering factors were modified to account for anomalous dispersion.[16] The final structural parameters and selected interatomic distances and angles are presented in Tables 2 and 3, respectively.

Discussion

Zeolite X is a synthetic counterpart of the naturally occurring mineral faujasite. The 14-hedron with 24 vertices known as the sodalite cavity or β-cage may be viewed as the principal building block of the aluminosilicate framework of the zeolite (see Figure 1). These β-cages are connected tetrahedral at six-rings by bridging oxygens to give double six-rings (D6R's, hexagonal prisms), and, concomitantly, to give an interconnected set of even larger cavities (supercages) accessible in three dimensions through 12-

Table 2. Positional, thermal, and occupancy parametersa for dehydrated Rb$_{71}$Na$_{21}$-X

Atom	Wyc. Pos.	x	y	z	[b]U$_{11}$ or [d]U$_{iso}$	U$_{22}$	U$_{33}$	U$_{12}$	U$_{13}$	U$_{23}$	[c]Occupancy Varied	[c]Occupancy Fixed
Si	96(g)	− 540(2)	343(2)	1239(3)	158(27)	118(26)	41(23)	23(29)	− 0(43)	− 1(39)		96
Al	96(g)	− 547(2)	1229(3)	360(2)	134(28)	1(24)	71(26)	− 14(42)	− 1(29)	− 33(40)		96
O(1)	96(g)	− 1080(4)	9(6)	1115(5)	36(79)	553(89)	224(98)	1(73)	− 15(56)	− 142(56)		96
O(2)	96(g)	63(6)	− 56(6)	1424(4)	182(73)	312(77)	149(81)	180(69)	− 136(71)	− 121(76)		96
O(3)	96(g)	− 351(4)	667(5)	704(5)	377(92)	105(81)	4(74)	15(75)	111(75)	20(66)		96
O(4)	96(g)	− 683(4)	753(5)	1722(5)	63(75)	136(75)	159(73)	− 117(78)	− 47(76)	− 9(60)		96
Rb(1)	16(c)	0	0	0	321(53)	321(53)	321(53)	103(72)	103(72)	103(72)	4.5(2)	4.5
Rb(2)	32(e)	801(4)	801(4)	801(4)	717(61)	717(61)	717(61)	− 87(74)	− 87(74)	− 87(74)	8.9(2)	9.0
Rb(3)	32(e)	1704(20)	1704(20)	1704(20)	648(145)	648(145)	648(145)	667(191)	667(191)	667(191)	2.6(2)	2.5
Rb(4)	32(e)	2539(2)	2539(2)	2539(2)	355(17)	355(17)	355(17)	88(27)	88(27)	88(27)	17.7(2)	18.0
Rb(5)	48(g)	1250	1250	4127(2)	1151(53)	1035(51)	204(31)	− 451(48)	0	0	32.9(3)	32.0
Rb(6)	96(g)	510(27)	556(27)	4320(22)	811(190)						5.2(3)	5.0
Na(1)	16(c)	0	0	0	321(53)	321(53)	321(53)	103(72)	103(72)	103(72)	7.0(2)	7.0
Na(2)	32(e)	2268(7)	2268(7)	2268(7)	279(101)						12.7(7)	14.0

[a]a=25.043(1) Å, space group Fd3̄, origin at center of symmetry. Positional and anisotropic thermal parameters are given × 10^4. Numbers in parentheses are the esd's in the units of the least significant digit given for the corresponding parameter. [b]The anisotropic temperature factor=exp[(− $2\pi^2/a^2)(U_{11}h^2+U_{22}k^2+U_{33}l^2+U_{12}hk+U_{13}hl+U_{23}kl$)]. [c]Occupancy factors are given as the number of atoms or ions per unit cell. [d]U$_{iso}$=(B$_{iso}$/8π^2).
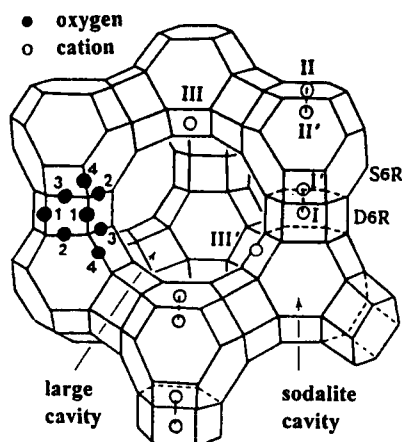
Figure 1. Framework structure of zeolite X. Near the center of the each line segment is an oxygen atom. The different oxygen atoms are indicated by number q to 4. Silicon and aluminum atoms alternate at the tetrahedral intersection, except that Si substitutes for about 4% of the Al's. Extraframework cation positions are labeled with Roman numerals.

ring (24-membered) windows. The Si and Al atoms occupy the vertices of these polyhedra. The oxygen atoms lie approximately half-way between each pair of Si and Al atoms, but are displaced from those points to give near tetrahedral angles about Si and Al.

Exchangeable cations, which balance the negative charge of the aluminosilicate framework, are found within the zeolite's cavities. They are usually found at the following sites shown in Figure 1: site I at the center of a D6R (alternatively called the hexagonal prism), site I' in the sodalite (β) cavity on the opposite side of one of the D6R's six-rings from site I, II' inside the sodalite cavity near a single six-ring (S6R entrance to the supercage, II in the supercage adjacent to a S6R, III in the supercage opposite a four-ring between two 12-rings, and III' somewhat off III (off the twofold axis).[17,18]

In this structure, seventy-one Rb$^+$ ions are found at six different crystallographic sites and twenty-one Na$^+$ ions are found two different crystallographic sites. Four and a half Rb$^+$ ions at Rb(1) and seven Na$^+$ ions at Na(1) lie at site I in the center of a D6R (see Figure 2). Each Rb$^+$ ion at Rb(1) (or each Na$^+$ ion at Na(1)) is coordinated by the six O(3) oxygen atoms of its D6R at distance of 2.578(12) Å, which is shorter than the sum of the ionic radii of Rb$^+$ and O^{2-}, 1.48+1.32=2.80 Å and longer than the sum of the ionic radii of Na$^+$ and O^{2-}, 0.97+1.32=2.29 Å.[13] The actual O(3)
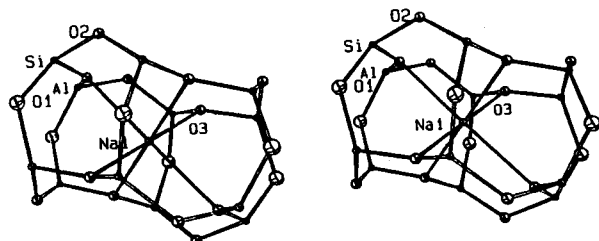
Figure 2. A stereoview of a D6R in dehydrated Rb$_{71}$Na$_{21}$-X. One Rb$^+$ ion at Rb(1) (site I) is shown. Ellipsoids of 20% probability are shown.
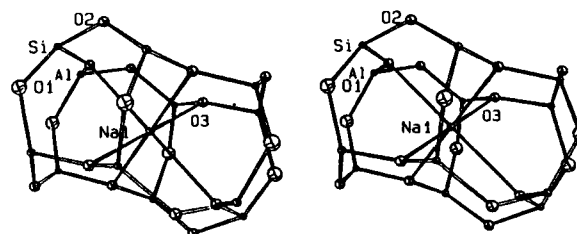
Figure 3. A stereoview of a D6R in dehydrated Rb$_{71}$Na$_{21}$-X. One Na$^+$ ion at Na(1) (site I) is shown. Ellipsoids of 20% probability are shown.

coordinates in a Rb$^+$ containing D6R must be somewhat different from those in a Na$^+$ containing D6R and this must lead to inaccuracies in both Na(1)-O(3) and Rb(1)-O(3) bond lengths. The former are likely to be shorter than the distance reported in Table 3 and the latter longer. The distances of Rb$^+$ to framework oxygens are similar distance between Rb$^+$ and framework oxygen (2.61(1) Å) in the structure of Rb$_{11}$Na$_1$-A.[19] In the hydrated RbNaX,[9] Rb$^+$ ions were found at site I. In this present dehydrated RbNaX, four and a half Rb$^+$ ions were also found at site I.

The Rb(2) position is at site I', on the threefold axis in the sodalite unit opposite D6Rs (see Figure 4) This is 32-fold position, but it is occupied by only nine Rb$^+$ ions. Each Rb$^+$ ion lies relatively far inside the sodalite cavity, 1.99 Å from the plane of the three O(3) framework oxygens of the D6R which it is bound. The Rb(2)-O(3) distance is 2.910 (15) Å, longer than the sum of the corresponding ionic radii, 1.48+1.32=2.80 Å. This indicates that Rb$^+$ ions coordinate weakly to their three O(3) oxygens.

Table 3. Selected interatomic distance (Å) and angles (deg)

Si-O(1)	1.617(12)	O(1)-Al-O(2)	108.9(7)
Si-O(2)	1.624(14)	O(1)-Al-O(3)	108.9(6)
Si-O(3)	1.634(13)	O(1)-Al-O(4)	109.1(6)
Si-O(4)	1.623(14)	O(2)-Al-O(3)	110.0(6)
Al-O(1)	1.734(14)	O(2)-Al-O(4)	108.0(7)
Al-O(2)	1.690(15)	O(3)-Al-O(4)	111.8(6)
Al-O(3)	1.719(14)	Si-O(1)-Al	127.7(8)
Al-O(4)	1.702(14)	Si-O(2)-Al	145.4(7)
Rb(1)-O(3)	2.578(12)	Si-O(3)-Al	137.1(8)
Rb(2)-O(3)	2.910(15)	Si-O(4)-Al	153.5(8)
Rb(3)-O(2)	3.105(37)	O(3)-Rb(1)-O(3)	90.6(4)
Rb(4)-O(2)	2.789(9)	O(3)-Rb(2)-O(3)	78.1(4)
Rb(5)-O(4)	2.918(12)	O(2)-Rb(3)-O(2)	80.6(5)
Rb(6)-O(1)	3.050(63)	O(2)-Rb(4)-O(2)	92.1(4)
Rb(6)-O(4)	2.960(57)	O(4)-Rb(5)-O(4)	71.9(4)
Na(1)-O(3)	2.578(12)	O(1)-Rb(6)-O(4)	54.0(6)
Na(2)-O(2)	2.350(19)	O(3)-Na(1)-O(3)	90.6(4)
		O(2)-Na(2)-O(2)	117.5(6)
O(1)-Si-O(2)	110.4(7)		
O(1)-Si-O(3)	110.0(7)		
O(1)-Si-O(4)	106.6(7)		
O(2)-Si-O(3)	77.5(5)		
O(2)-Si-O(4)	109.7(7)		
O(3)-Si-O(4)	111.1(7)		

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

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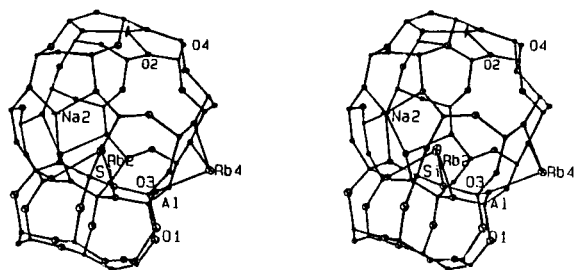
Figure 4. A stereoview of a sodalite cavity with an attached D 6R in dehydrated $Rb_{71}Na_{21}$-X. One Rb^+ ion at Rb(2) (site I') and two Rb^+ ions at Rb(4) (site II) and two Na^+ ions at Na(2) (site II) are shown. About 75% of the sodalite cavities may have this arrangement. Ellipsoids of 20% probability are shown.
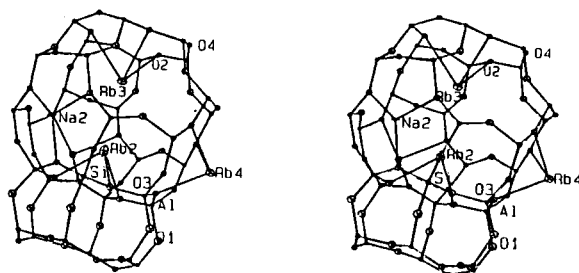
Figure 5. A stereoview of a sodalite cavity with an attached D 6R in dehydrated $Na_{21}Rb_{71}$-X. One Rb^+ ion at Rb(2) (site I') and one Rb^+ ion at Rb(3) (site II') and two Rb^+ ions at Rb(4) (site II) and one Na^+ ion at Na(2) (site II) are shown. About 25% of the sodalite cavities may have this arrangement. Ellipsoids of 20% probability are shown.

Two and a half Rb^+ ions lie at Rb(3). Rb(3) is recessed *ca*. 2.06(2) Å into sodalite cavity from the S6R plane at O (2) (see Figure 5 and Table 4). Each of these Rb^+ ions coordinates to three O(2) oxygens at 3.11 Å. Rb(4) is recessed ca 1.55(1) Å into the supercage from the S6R plane at O(2) and Na(2) is recessed ca 0.38(1) Å into the supercage from the S6R plane at O(2) (see Figure 6, Table 4). Eighteen Rb^+ ions lie at Rb(4) (site II). The Rb(4)-O(2) distance, 2.789(9) Å, is almost the same as the sum of ionic radii of Rb^+ and O^{2-}, 1.48+1.32=2.80 Å.

Thirty-two Rb^+ ions at Rb(5) per unit cell (4 per supercage) occupy the 48-fold position at site III in the supercages (see Figure 6). The Rb(5)-O(4) distance is 2.918 (12) Å. Five Rb^+ ions at Rb(6) per unit cell lie in the su-
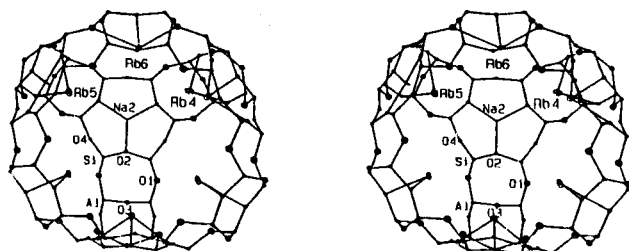
Figure 6. A stereoview of supercage of dehydrated $Rb_{71}Na_{21}$-X. Two Rb^+ ions at Rb(4) (site II) and two Na^+ ions at Na(2) (site II) and four Rb^+ ions at Rb(5) (site III) and one Rb^+ ion at Rb(6) (site III') are shown. About 75% of the supercages have this arrangement. Ellipsoids of 20% probability are shown.

Table 4. Deviations (Å) of atoms from the 6-ring oxygen planes

		Dehydrated $Rb_{71}Na_{21}$-X
at $O(2)^a$	Rb(3)	$-2.26(1)$
	Rb(4)	1.60(1)
	Na(2)	0.34(1)
at $O(3)^b$	Rb(2)	1.99(1)

^{a}A positive deviation indicates that the atom lies in the supercage.
^{b}A positive deviation indicates that the atom lies in the sodalite cavity.

percage at site III'. The ions at Rb(6) bind to six framework oxygens (to two O(4)'s at 2.96(6) Å and to four O(1)'s at 3.05(6) Å) (see Figure 6 and Table 3).

The Na(2) and Rb(4) occupy site II in the supercage with occuancies of 14 and 18, respectively, filling this 32-fold e-quipoint. Na(2)-O(2) is 2.350(19) Å, which is a little longer than the sum of the ionic radii of Na^+ and O^2, 0.97+1.32= 2.29 Å, and O(2)-Na(2)-O(2) is 117.5(6)°; Rb(4)-O(2) is 2.79 Å which is almost the same as the sum of the ionic radii of Rb^+ and O^{2-}, 2.80 Å, and O(2)-Rb(4)-O(2) is 92.1(4). The 14 Na^+ ions at Na(2) are only 0.34 Å from the plane of the single six-ring; 18 Rb^+ ions at Rb(4) are much further, 1.66 Å from the corresponding plane. Plausible ionic arrangements for a sodalite unit and a supercage are shown in Figures 4, 5, and 6.

Recently the crystal structures of dehydrated K_{92}-X,[5] Tl_{92}-X,[6] Cd_{46}-X,[20] Sr_{46}-X,[21] Mn_{46}-X,[22] Mg_{46}-X,[23] Ba_{46}-X,[23] and $Ca_{32}K_{28}$-X,[24] have been determined. The divalent cations, Ca^{2+}, Cd^{2+}, Sr^{2+}, and Mn^{2+} ions are located at two different sites of high occupancies: sixteen at site I and thirty at site II. In the crystal structures of the Ba_{46}-X and Mg_{46}-X,[23] Ba^{2+} and Mg^{2+} ions are located at the three different sites; fourteen at site I, two at site I', and 30 at site II. In the crystal structure of $Ca_{32}K_{28}$-X, smaller Ca^{2+} ions occupy the smaller pore site (16 at site I and 16 at site II) and larger K^+ ions occupy deep in the supercage (16 at sites II and 12 at III). In the crystal structure Tl_{92}-X,[6] ninety-two Tl^+ ions are distributed in the four different crystallographic site; 32 at site I', 32 at site II, about 16 at III' site, and the remainder (about 12) at another III' site.

Koller *et al.*[25] studied the location of Na^+ and Cs^+ cations inside the dehydrated $Cs_{40}Na_{15}$-Y by solid state ^{23}Na and ^{133}Cs nuclear magnetic resonance (NMR) spectroscopy and Rietveld method. They found Na^+ cations at site I are replaced by Cs^+ cations at high cesium exchange level. Upon increasing the calcination temperature of the $Cs_{40}Na_{15}$-Y from 473 to 773 K, further migration of Cs^+ and Na^+ to site I is observed. Even though the ionic radius of Cs^+ is 1.67 Å, Cs^+ ion can occupy at site I. Their results are in good agree-

Table 5. Distribution of nonframework atoms over sites

Site	
I	4.5 Rb, 7.0 Na
I'	9.0 Rb
II	18.0 Rb, 14.0 Na
II'	2.5 Rb
III	32.0 Rb
III'	8.0 Rb

ment with the present work.

In this work, fully Rb$^+$-exchanged zeolite X was not successfully prepared. Seventy-one Rb$^+$ ions and 21 Na$^+$ ions are distributed in the seven different crystallographic sites; four and a half Rb$^+$ ions and seven Na$^+$ ions at site I, nine Rb$^+$ ions at site I', 18 Rb$^+$ ions at site II, two and a half Rb$^+$ ions and 14 Na$^+$ ions at site II', 32 Rb$^+$ ions at site III, and five Rb$^+$ ions at site III'.

Supplementary Material Available. Tables of calculated and observed structure factors with esd's (5 pages). Ordering information is given on any current masthead page.

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Tautomeric and *Ab Initio* Studies of 5-Thioxo-3*H*,4*H*-1,3,4-thiadiazolidin-2-one

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The oxidation product bis(2-oxo-3*H*-1,3,4-thiadiazolidinyl)-5,5-disulfide (**5b**) was obtained from an attempted synthesis of 5-thioxo-3*H*,4*H*-1,3,4-thiadiazolidin-2-one (**1**). Spectroscopic results indicate that the most stable tautomeric form of **1** is the lactam-thiol form (**1b**). The computed total energies and relative energies at the MP4 level also showed that the most stable tautomer is **1b**.

Introduction

In light of the biological and analytical interest in 3*H*-1,3,4-thiadiazolines, we recently reported the synthesis and tautomeric behaviour of 5-amino-3*H*-1,3,4-thiadiazoline-2-thione[1] and 5-amino-3*H*-1,3,4-thiadiazolin-2-one.[2,3] 5-Amino-3*H*-1,3,4-thiadiazoline-2-thione and 5-aroylamino-3*H*-1,3,4-thiadiazoline-2-thiones can exist in two-tautomeric forms a thione form, and a thiol form. It was established that 5-amino-3*H*-1,3,4-thiadiazoline-3-thione and 5-aroylamino-3*H*-

1,3,4-thiadiazoline-2-thiones exist in their thione form on the basis of ^{1}H NMR, ^{13}C NMR and IR spectral data.[1] Similarly, a stable tautomeric structure for 5-amino-3*H*-1,3,4-thiadiazolin-2-one and 5-aroylamino-3*H*-1,3,4-thiadiazolin-2-ones was proven to be the lactam form.[2] As an extension of these studies, we report our synthetic and tautomeric results for 5-thioxo-3*H*,4*H*-1,3,4-thiadiazolidin-2-one (**1**) on the basis of experimental spectral data and theoretical calculations.

5-Thioxo-3*H*,4*H*-1,3,4-thiadiazolidin-2-one is not a known compound. However, 3*H*,4*H*-1,3,4-thiadiazolidine-2,5-dione