

# Crystal Structure of a Sodium Sorption Complex of Zeolite X Containing Linear $\text{Na}_3^{2+}$ Clusters

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An anhydrous single crystal of sodium zeolite X,  $\text{Na}_{92}\text{Si}_{100}\text{Al}_{92}\text{O}_{384}$ , was exposed for 48 h to Na vapor at 225 °C. Its structure was determined by X-ray diffraction methods in the cubic space group  $Fd\bar{3}$ ;  $a = 25.100(11)$  Å at 22 °C;  $R_1 = 0.071$  and  $R_2 = 0.088$  for the 544 reflections for which  $I > 3\sigma(I)$ . A total of 106 sodiums are found per unit cell, 14 more than the number of  $\text{Na}^+$  ions required to balance the negative charge of the zeolite framework. The same number, 14, of Na atoms are found at the very centers of 12-oxygen rings, far from the zeolite framework. It appears that each Na atom has been captured by a pair of  $\text{Na}^+$  ions to form linear  $\text{Na}_3^{2+}$  clusters that nearly fill the 12-oxygen rings. Each terminal sodium approaches two oxygens of an  $\text{AlO}_4$  tetrahedron of the zeolite framework with Na–O distances of 2.33(3) and 2.83(4) Å. Although some delocalization of the single valence electron over this cluster must occur, it is recognized, from the sodium approach distances to framework oxygens, that the terminal sodiums are largely cationic and the central sodium is closer to neutral. The bond lengths in the cluster are 2.93(3) Å, about the same as the corresponding distance in  $\text{Na}_5^{4+}$ , 2.80(2) Å, and the sum of the radii of  $\text{Na}^0$  and  $\text{Na}^+$ , 2.83 Å.

## Introduction

When zeolites containing alkali-metal cations are exposed to an alkali-metal vapor, sorption,<sup>1–7</sup> and sometimes redox reaction,<sup>8–12</sup> can occur. When excess atoms are sorbed, their valence electrons delocalize to various degrees to form cationic clusters within the cavities of the zeolite. Such clusters were originally produced in low concentration by  $\gamma$ -irradiation.<sup>13</sup> To achieve higher (stoichiometric) concentrations, the alkali metal itself may be used. It may be introduced neat or in situ by the decomposition of the azide (for sodium).<sup>14</sup> More recently, Yoon et al. have introduced alkali-metal atoms into zeolite Y by direct grinding of the zeolite and the metal in a glovebox and by using solutions of alkali metals in 18-crown-6 ether/tetrahydrofuran.<sup>15</sup> At lower loadings various small cationic clusters can form inside zeolites, but at higher loadings cationic continua that can fill the cavities may form. These novel materials are likely to have unique properties that may lead to applications in electronics and materials science.<sup>1,7</sup>

ESR work has led to the identification of a number of such clusters. Kasai and Rabo<sup>13,16–18</sup> were the first to characterize the small cationic clusters  $\text{Na}_4^{3+}$  and to identify the larger sodium “metallic” clusters in dehydrated zeolite Y powder exposed to sodium metal vapor. In zeolite X powder, they identified  $\text{Na}_6^{5+}$  (less certainly) and the larger “metallic” clusters.<sup>15</sup> Subsequently, a series of ESR experiments were done by Edwards et al.,<sup>1</sup> Martens et al.,<sup>19</sup> and Kevan et al.<sup>14</sup> on zeolites prepared by various synthetic methods. Edwards confirmed the existence of the  $\text{Na}_4^{3+}$  cationic alkali metal cluster and found the  $\text{Na}_5^{4+}$  and  $\text{Na}_6^{5+}$  clusters in zeolite Na-X and Na-Y. Subsequently, the alkali metal clusters  $\text{Na}_4^{3+}$ ,  $\text{K}_4^{3+}$ , and  $\text{K}_3^{2+}$ , as well as “metal particles” (actually larger cationic clusters) of Na, K, Rb, and Cs were identified in zeolites A, X, and Y. Recent reviews of cationic sodium clusters<sup>20</sup> in zeolites and, more generally, of alkali-metal clusters<sup>7</sup> are available.

Crystallographic findings have led to an increased understanding of the diversity of alkali-metal clusters that can form within zeolites.<sup>2,12</sup> Seff and co-workers identified the new alkali

metal clusters  $\text{Cs}_4^{3+}$ ,  $\text{Cs}_3^{2+}$ , and  $\text{Rb}_6^{4+}$  and determined their structures and placement within zeolite A.<sup>10,21,22</sup> They did the same for the  $\text{K}_4^{3+}$  and  $\text{K}_3^{2+}$  clusters in zeolite A<sup>2,5</sup> and for the  $\text{Na}_5^{4+}$  cluster in zeolite X.<sup>12</sup> A novel cationic continuum of cesium atoms and ions was synthesized in zeolite X by Sun and Seff,<sup>3</sup> who determined its structure. The structures of  $\text{Na}_4^{3+}$  and  $\text{Cs}_4^{2+}$  were determined by Edwards et al.<sup>6</sup> and Armstrong et al.,<sup>4</sup> respectively.

Both crystallography and ESR have inherent limitations in the characterization of intrazeolitic clusters. The limitations of crystallography are that (1) only geometrical information, and only the electronic information that can be inferred from geometry, can be obtained, (2) only clusters present in high concentration can be identified, and (3) only clusters at positions of relatively high symmetry can be confirmed without ambiguity.

The severe limitation of ESR is that it can do no more than recognize that a number of nuclei may be structurally equivalent. If nuclei that are not structurally equivalent are exchanging rapidly (faster than the time scale of the ESR experiment, ca.  $10^{-4}$  s), they will still appear to be structurally equivalent. Even with the firm information, never available from ESR alone, that a group of nuclei are structurally equivalent, conclusions regarding the shape and symmetry of the cluster, or of its location within the zeolite, are tenuous, and interatomic distances cannot be estimated at all. To date, the largest cluster to be identified by ESR has six nuclei that appear to be equivalent, but a likely structure and position for such a cluster in its host zeolite are not apparent, suggesting that rapid exchange is occurring. Substantially larger clusters or continua give only a single-line spectrum like that of the bulk metal and so cannot be further identified. Finally, if a cluster does not have an unpaired electron, it cannot be identified by ESR.

The two physical methods, crystallography and ESR, are sometimes not as complementary as they could be in the study of zeolites because of the problem of preparing exactly the same materials for study by both methods, especially if single-crystal and powder results are to be compared, or if powder samples are not pure or uniform.

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This work was done to determine the structures of some sodium clusters in zeolite X. It was hoped that enough sodium would be absorbed to form a cationic sodium continuum, like the cesium continuum that resulted when Na-X was exposed to Cs gas.<sup>3</sup>

### Experimental Section

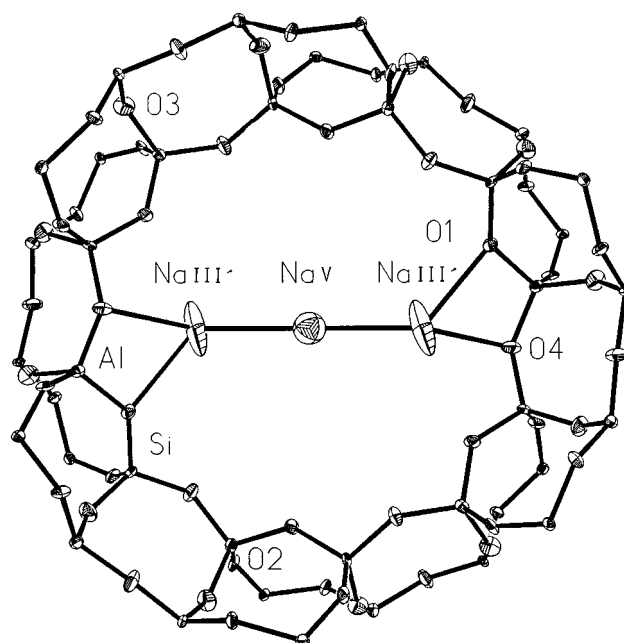
Large single crystals of sodium zeolite X, of stoichiometry  $\text{Na}_{92}\text{Si}_{100}\text{Al}_{92}\text{O}_{384}$  per unit cell, were prepared in St. Petersburg, Russia.<sup>23</sup> One of these, a colorless octahedron about 0.25 mm in cross section, was lodged in a fine Pyrex capillary. After complete dehydration at 400 °C and  $1 \times 10^{-5}$  Torr for 48 h, sodium (99.98% purity, Johnson Matthey Inc.) was introduced by distillation from a sidearm break-seal ampule to the Pyrex-tube extension of the crystal-containing capillary. This reaction vessel was then sealed off under vacuum and placed in a long horizontal cylindrical oven. The reaction was carried out at 225 °C for 48 h with  $4.7 \times 10^{-4}$  Torr of sodium vapor. This vapor pressure is quite low. Vapor diffusion in the fine capillary through residual gas (Hg, N<sub>2</sub>, etc.) must therefore have been a consideration; it was seen to have limited the extent of alkali-metal sorption by the zeolite. After cooling to room temperature, the clear colorless perhaps faintly amber crystal, still under vacuum in its capillary, was sealed off from the reaction vessel by torch.

Additional observations are offered to support the integrity of the sorption experiment. The good initial vacuum achieved indicates that the system contained no leaks. No evidence for failures at seal-off points was seen. These, when they occurred, caused the sodium metal to lose its surface luster and caused opaque white-to-black deposits to form. Such experiments were discontinued. In leak-free experiments, the inner walls of the reaction vessels were seen after reaction to be tinted brown-black, grading to colorless at the capillary tip. This showed that Na(g) had been present to react with the Pyrex and with any traces of H<sub>2</sub>O or O<sub>2</sub> that may have remained. It also showed that the Na<sup>0</sup> concentration decreased with the distance from its source to the tip as would be expected owing to diffusion through residual gas. Finally, two crystals, each in its own capillary, were prepared in parallel. The other became black presumably because the crystal was closer to the sodium source (35 vs 75 mm) and much further from the end of the capillary (60 vs 18 mm) where residual gases (initially ca.  $1 \times 10^{-5}$  Torr at 225 °C) can be expected to have been compressed by Na(g) ( $47 \times 10^{-5}$  Torr at 225 °C) as the reaction vessel was heated. That the structure was the same when determined with diffraction data gathered 2 and 124 weeks after the crystal was sealed in its capillary argues for the integrity of this final seal-off.

The cell constant, 25.100(11) Å, was determined by a least-squares treatment of 20 intense reflections for which  $18^\circ < 2\theta < 30^\circ$ . The  $\theta$ - $2\theta$  scan technique was used for data collection using Mo K $\alpha$  radiation ( $\lambda_1 = 0.70930$ ,  $\lambda_2 = 0.71359$  Å). Each reflection for which  $4^\circ < 2\theta < 45^\circ$  was scanned at a constant rate of  $1.0^\circ \text{ min}^{-1}$  in  $\omega$  from  $0.5^\circ$  below the K $\alpha_1$  peak to  $0.5^\circ$  above the K $\alpha_2$  maximum. Background intensity was counted at each end of a scan range for a time equal to one-half the scan time. The intensities of three reflections in diverse regions of reciprocal space were recorded every 97 reflections to monitor crystal and instrument stability. Only small random fluctuations of these check reflections were observed.

Standard deviations were assigned to individual reflections by

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



**Figure 1.** Linear  $\text{Na}_3^{2+}$  cluster within a 12-oxygen (24-membered) ring. By their distances from the zeolite framework, the central sodium (at site V) should be more like an atom than a cation and the terminal sodiums (at sites III') should be more cationic. Still, it is expected that significant delocalization of the single valence electron over the length of the cluster has occurred. The cluster is shown at one of the three positions it can occupy, extending from one  $\text{AlO}_4$  group to its opposite  $\text{AlO}_4$ . Ellipsoids of 20% probability are shown.

where CT is the total integrated count,  $B_1$  and  $B_2$  are the background counts, and  $I$  is the intensity. The value of  $p$  converged to 0.004 in the final refinement of the structure. 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. Because the crystal was a regular octahedron with no heavy atoms, it was decided that an absorption correction was unnecessary. Diffraction data were collected with an automated Siemens four-circle computer-controlled P3 diffractometer. Of the 1635 reflections gathered, 1058 of which were independent (merging  $R = 0.076$ ), only the 544 for which the net count exceeded 3 times its standard deviation were used in subsequent structure determination and refinement. The crystal structure was solved in the cubic space group  $Fd\bar{3}$ , consistent with systematic absences, the intensity inequalities  $I_{hkl} \neq I_{khl}$ , and previous determinations using crystals from the same batch. This requires that the Si and Al atoms alternate as shown in Figure 1; Loewenstein's rule<sup>24</sup> is obeyed.

### Structure Determination

Full-matrix least-squares refinement was initiated using framework coordinates obtained from Olson's determination of the structure of dehydrated Na-X.<sup>25</sup> These positions when refined anisotropically yielded  $R_1 = 0.23$  and  $R_2 = 0.32$ , where

$$R_1 = \sum |F_o - |F_c|| / \sum F_o$$

and

$$R_2 = (\sum w(F_o - |F_o|)^2 / \sum wF_o^2)^{1/2}$$

A Fourier difference function yielded two strong peaks at (0.05, 0.05, 0.05) and (0.25, 0.25, 0.25), positions near framework oxygens normally occupied by Na<sup>+</sup> ions. Refine-

TABLE 1: Positional, Thermal, and Occupancy Parameters<sup>a</sup>

atom	wyc pos	x	y	z	$U_{11}^b$ or $U$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$	occupancy <sup>c</sup>	
											varied	fixed
Si	96(g)	-545(1)	1258(1)	348(1)	20(2)	16(2)	14(2)	-4(2)	1(1)	-3(2)		96
Al	96(g)	-556(1)	363(1)	1241(2)	21(2)	14(2)	18(2)	2(1)	-4(2)	-4(2)		96
O(1)	96(g)	-1111(3)	2(3)	1062(3)	36(6)	48(6)	29(5)	-9(5)	-6(4)	-3(4)		96
O(2)	96(g)	-13(3)	-26(3)	1407(3)	19(4)	22(4)	26(5)	1(4)	-15(4)	-15(4)		96
O(3)	96(g)	-356(3)	748(3)	706(3)	33(5)	31(5)	32(5)	1(4)	3(4)	10(4)		96
O(4)	96(g)	-694(3)	721(3)	1805(3)	33(5)	28(5)	28(5)	12(4)	-10(4)	-16(4)		96
Na(I')	32(e)	480(3)	480(3)	480(3)	48(5)	48(5)	48(5)	1(4)	1(4)	1(4)	27.3(10)	
Na(II)	32(e)	2292(3)	2292(3)	2292(3)	35(4)	35(4)	35(4)	17(3)	17(3)	17(3)	29.3(9)	
Na(III')	96(g)	4076(9)	421(39)	493(19)	17(3)	199(40)	310(54)	2(18)	-28(22)	-136(36)	28.1(15)	
Na(V)	16(d)	5000	5000	5000	162(16)						14.1(8) <sup>d</sup>	

<sup>a</sup>  $a = 25.100(11)$  Å, space group  $Fd\bar{3}$ , origin at center. Positional and thermal parameters (Å<sup>2</sup>) are given  $\times 10^4$ , respectively. Numbers in parentheses are the esd's in the units of the least significant digit given for the corresponding parameter. <sup>b</sup> The anisotropic temperature factor =  $\exp[-2\pi^2/a^2(U_{11}h^2 + U_{22}k^2 + U_{33}l^2 + 2U_{12}hk + 2U_{13}hl + 2U_{23}kl)]$ . <sup>c</sup> Occupancy factors are given as the number of atoms or ions per unit cell. <sup>d</sup> Constrained to be one-half of the occupancy at Na(III'). These two values are approximately the same as those resulting from free refinement.

ment of these positions with only occupancy and isotropic thermal parameters varying led to an occupancy at (0.05, 0.05, 0.05) (see Table 1), which was a little too high, so it was reset and fixed at 0.333 (full occupancy). Subsequently, the structure refined to  $R_1 = 0.13$  and  $R_2 = 0.17$ .

Two more peaks were found at the special positions (0.675, 0.125, 0.125) and (0.125, 0.125, 0.125). These positions, not normally occupied by sodium ions, diverged when put into refinement. From the Fourier function, a peak at (0.41, 0.042, 0.059) was put into refinement. Positions such as this, at or near site III, are common cation sites in zeolite X; Olson found three such sites occupied in dehydrated Na<sub>88</sub>-X.<sup>25</sup> Five cycles of refinement resulted in  $R_1 = 0.12$  and  $R_2 = 0.15$ . Occupancy at this site III' converged to 28(2) with III' to framework-oxygen bonds, 2.46 Å in length, similar to that found in Olson's dehydrated Na-X structure.<sup>25</sup> This distance is too short for III' to represent water oxygens. (This is a test for possible experimental error; no water could have survived the steps of dehydration and exposure to Na(g).) These site-III' Na<sup>+</sup> ions are of the number needed to complete the count to balance the negative charge of the zeolite framework.

An ensuing Fourier function revealed a strong peak at the special position (0.5, 0.5, 0.5), site V, a position of symmetry  $\bar{3}$  at the center of the 12-ring. This was refined as Na<sup>0</sup> with an isotropic temperature factor to  $R_1 = 0.095$  and  $R_2 = 0.099$ . This position is about 2.9 Å from Na<sup>+</sup> at site III', a distance near that in Na<sub>5</sub><sup>4+</sup>.<sup>12</sup> This sodium in the middle of the 12-ring is very far, 5.5 Å, from the nearest atoms of the anionic zeolite framework, so it appears to be a neutral atom, Na<sup>0</sup>, again as in Na<sub>5</sub><sup>4+</sup>. Also, enough Na<sup>+</sup> ions had already been found to balance the framework charge. Refining Na(V) as an oxygen atom, representing perhaps a water molecule (another test for possible experimental error), led to a negative (unrealistic) thermal parameter and increased  $R$  values. In addition, the III'-V distance, 2.93(3) Å, is about half an angstrom too long to be a Na<sup>+</sup>-O coordination distance. Beyond that, both H<sub>2</sub>O and its possible hydrolysis product, OH<sup>-</sup>, would be expected to appear at sites where they could hydrogen bond to framework oxygens in addition to coordinating at normal distances to Na<sup>+</sup> ions.

Because the occupancy at site V was refining closely to half that at III' (14(1) Na<sup>0</sup> and 25(3) Na<sup>+</sup>, respectively), this was introduced as a constraint. Refinement to convergence with this constraint led to  $R_1 = 0.091$  and  $R_2 = 0.090$ .

Anisotropic refinement of this structure, except for Na(V), which was refined isotropically, led to the final  $R_1$  and  $R_2$  values of 0.071 and 0.088, respectively. The shifts in the final cycle of least-squares refinement were less than 0.1% of their

TABLE 2: Selected Bond Distances (Å) and Angles (deg)

	bond distances (Å)		bond angles (deg)
Si-O(1)	1.610(9)	O(1)-Si-O(2)	113.1(4)
Si-O(2)	1.630(8)	O(1)-Si-O(3)	110.9(5)
Si-O(3)	1.632(9)	O(1)-Si-O(4)	107.0(5)
Si-O(4)	1.617(9)	O(2)-Si-O(3)	104.7(4)
Al-O(1)	1.722(9)	O(2)-Si-O(4)	107.3(4)
Al-O(2)	1.729(8)	O(3)-Si-O(4)	113.9(4)
Al-O(3)	1.729(9)	O(1)-Al-O(2)	113.9(4)
Al-O(4)	1.711(9)	O(1)-Al-O(3)	109.0(4)
Na(I')-O(3)	2.276(9)	O(1)-Al-O(4)	109.1(4)
Na(I')-O(2)	2.925(7)	O(2)-Al-O(3)	106.0(4)
Na(II)-O(2)	2.363(8)	O(2)-Al-O(4)	104.9(4)
Na(II)-O(4)	2.878(9)	O(3)-Al-O(4)	114.1(4)
Na(III')-O(4)	2.33(3)	Si-O(1)-Al	133.0(5)
Na(III')-O(1)	2.84(4)	Si-O(2)-Al	146.5(5)
Na(III')-Na(V)	2.93(3)	Si-O(3)-Al	141.3(6)
		Si-O(4)-Al	145.4(6)
		O(3)-Na(I')-O(3)	115.4(3)
		O(2)-Na(II)-O(2)	113.3(3)
		O(1)-Na(III')-O(4)	62.9(9)
		Na(III')-Na(V)-Na(III')	180 <sup>a</sup>

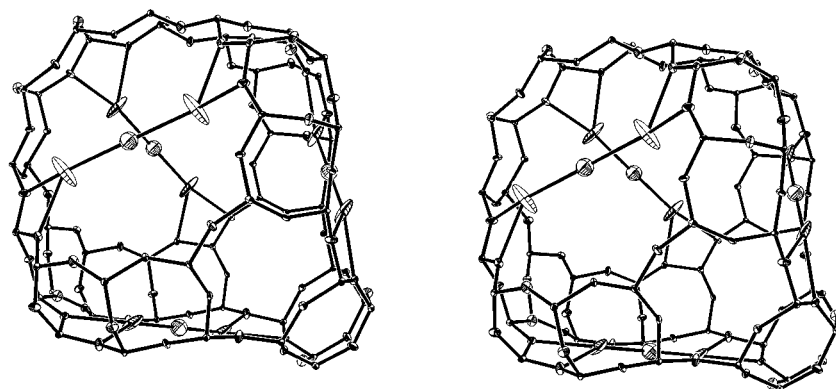
<sup>a</sup> Exactly by symmetry.

corresponding standard deviations. (When Na(V) was removed from refinement,  $R_1$  and  $R_2$  converged to the sharply increased values of 0.094 and 0.132, respectively. Na(V), when refined anisotropically, converged to the still positive-definite thermal parameters  $U_{ii} = 0.0011(2)$  and  $U_{ij} = -0.0016(16)$  Å<sup>2</sup>.)

The goodness-of-fit,  $[\sum w(F_o - |F_c|)^2/(m - s)]^{1/2}$ , is 2.55; the number of observations,  $m$ , is 544, and the number of parameters,  $s$ , is 80. The largest maximum/minimum in the final difference function is 0.9/-0.7 e Å<sup>-3</sup>. Atomic scattering factors for Si, Al, O, and Na were used. (Using the Na<sup>+</sup> scattering factor in structure refinement for sodiums at sites other than site V had no significant effect on bond lengths or occupancies.) All scattering factors<sup>26,27</sup> were modified to account for anomalous dispersion. The final structural parameters are presented in Table 1 and selected interatomic distances and angles are in Table 2.

## Discussion

Near-full occupancy (27.3(10) Na<sup>+</sup> ions) is seen at site I', a 32-fold position located in the sodalite cavity opposite a double six-ring. Similar near-full occupancy (29.0(9) Na<sup>+</sup> ions) is seen near the centers of the single six-rings at site II, also a 32-fold position. Sodium found at sites I' and II have bond distances to framework oxygens (see Table 3) similar to those previously reported.<sup>25</sup>



**Figure 2.** Stereoview of a supercage in the structure of  $\text{Na}_{92}\text{-X}\cdot 14\text{Na}$ . Four 12-rings are arranged tetrahedrally about its center at (0.375, 0.375, 0.375). Each 12-ring is spanned by a linear  $\text{Na}_3^{2+}$  cluster. Half of the supercages have all of their 12-rings filled as shown; the remainder have one 12-ring vacant. (In zeolite X with  $\text{Si}/\text{Al} = 1.00$ , all should be occupied as shown.) The orientation of each cluster in each ring is selected from among the possibilities to avoid the shortest  $\text{Na}_3^{2+}\text{--Na}_3^{2+}$  distances. Ellipsoids of 20% probability are shown.

**TABLE 3: Comparison of Selected Bond Lengths (Å) in Anhydrous Na-X<sup>a</sup> and its  $\text{Na}_3^{2+}$  Complex**

	Na-X	this work
$\text{Na(I')}-\text{O(3)}$	2.242(7)	2.276(9)
$\text{Na(I')}-\text{O(2)}$	2.942(6)	2.925(7)
$\text{Na(II)}-\text{O(2)}$	2.343(5)	2.363(8)
$\text{Na(II)}-\text{O(4)}$	2.887(5)	2.878(9)
$\text{Na(III')a}-\text{O(4)}^b$	2.22(5)	2.33(3)
$\text{Na(III')a}-\text{O(1)}$	2.85(6)	2.84(4)
$\text{Na(III')b}-\text{O(4)}$	2.58(5)	
$\text{Na(III')b}-\text{O(1)}$	3.61(4)	
$\text{Na(III')c}-\text{O(4)}$	2.41(5)	
$\text{Na(III')c}-\text{O(1)}$	2.44(5)	

<sup>a</sup> See ref 25. <sup>b</sup> Olson (ref 25) found  $\text{Na}^+$  ions at three different sites III'. These are designated Na(III')a, Na(III')b, and Na(III')c above.

The remaining  $\text{Na}^+$  ions are nicely found at site III', a general position inside the supercage opposite four-rings. This 96-fold position is only partially occupied (28(2)  $\text{Na}^+$  ions). These Na(III')s, by their relatively long approach distances to framework oxygens (2.33(3) and 2.83(4) Å) compared to the sum of the ionic radii ( $0.97 + 1.32 = 2.29$  Å), appear to be less positively charged than  $\text{Na}^+$ . This is indicative of some delocalization of electron density from  $\text{Na}^0$  at site V to the  $\text{Na}^+$  ions at site III'; these would be bonding interactions.

Assuming that sites I' and II are fully occupied, a total of about 106.2 Na's are found per unit cell in this structure. The initial number of  $\text{Na}^+$  cations, those needed to balance the charge of the anionic framework, is 92. By difference, then, there should be about  $106.2 - 92 = 14.2$  Na atoms per unit cell. Refinement shows that approximately that many, 14.1(8), Na's exist at site V, a site very far from the anionic zeolite framework and therefore suitable for  $\text{Na}^0$ .

Site V, at the center of the 12-oxygen ring, is not a conventional cation site in dehydrated FAU. However, hydrated  $\text{Ce}^{3+}$  and  $\text{La}^{3+}$  ions, probably hydrolyzed, are found at this site in hydrated ion-exchanged natural FAU and zeolite X, respectively.<sup>28</sup>

There are twice as many  $\text{Na}^+$  ions at site III' (an average of nearly two distributed over the six sites per 12-ring) as atoms at site V (nearly one per 12-ring). This indicates, but does not prove, that each Na atom is held in place by two  $\text{Na}^+$  ions. This "two" could be an average value; some 12-rings could have only one  $\text{Na}^+$  (or zero) and others could have three (or four, five, or six) to give, fortuitously, an average of two.

However, an atom would not be expected to occupy a position as special as site V unless the III'  $\text{Na}^+$  ions to which it bonds are arranged symmetrically about it. If the "two" of the previous paragraph is an average, then one of its components must be

one or zero, neither of which would support a  $\text{Na}^0$  atom at its position. One may conclude that each  $\text{Na}^0$  is held in place by two  $\text{Na}^+$  ions.

This point may be argued alternatively as follows.  $\text{Na}^+$  ions should not be placed at adjacent III' sites in 12-rings. They would be too close together, 2.93(4) Å, and it would be unreasonable to place cations so close when much longer distances are readily available. Therefore, no 12-ring should contain four, five, or six  $\text{Na}^+$  ions. Any with three should have them arranged trigonally. Any with two should have them opposite ("para" or "1, 4") or "meta" ("1, 3") but not "ortho." Perhaps "para" is best.

Of all of these, only the structure with two  $\text{Na}^+$  ions opposite can capture and hold a Na atom at the 12-ring center. One or zero  $\text{Na}^+$  ions would not. Three  $\text{Na}^+$  ions could capture a Na atom but not at the 12-ring center because III' sites do not lie in 12-ring planes; three III' sites arranged trigonally would all be displaced to one side or the other of the 12-ring plane. The final alternative, of two  $\text{Na}^+$  ions occupying sites III' at "meta" or "1, 3" sites, would also not constrain Na(V) to be firmly at the center of the 12-ring. Thus, it may be concluded that each  $\text{Na}^0$  at site V is bound to two site-III'  $\text{Na}^+$  ions to form a linear cluster.

Ab initio molecular dynamics calculations have been performed on cluster formation in sodium-doped Na-Y modeled with a fixed arrangement of silicon and aluminum ions.<sup>20</sup> (Na-Y differs from Na-X only in the Si/Al ratio of its framework and, therefore, in framework charge and in the number of ions that are needed to balance it.) A  $\text{Na}_3^{2+}$  cluster was identified in a 12-ring in that work, but it was far from linear. Perhaps the 12-ring used in the model did not have a pair of aluminums opposite.

Site V is a 16-fold position at the 12-ring centers, between two supercages. Because it is very far (5.5 Å) from the nearest framework oxygens, the Na's there should not have much positive charge. (Fully or near-fully charged  $\text{Na}^+$  cations would approach anionic framework oxygens more closely; they would be expected to occupy the remaining III' sites.) Also, the III'–V bond distance, 2.93(4) Å, is far too short to be a  $\text{Na}^+ \text{--} \text{Na}^+$  interaction. This distance indicates that some moderating (bonding) electron density is present. Each  $\text{Na}_3^{2+}$  cluster bridges through and across a 12-ring from two oxygens of one anionic "AlO<sub>4</sub>" tetrahedron to the corresponding two oxygens of the opposite tetrahedron (see Figure 1). To form  $\text{Na}_3^{2+}$  clusters, the 28  $\text{Na}^+$  ions at III' should be able to accept only 14  $\text{Na}^0$  atoms at site V, leaving this 16-fold position somewhat less than full, just as is found (14.1(8) Na's).

Zeolite X of composition  $\text{Na}_{96}\text{Si}_{96}\text{Al}_{96}\text{O}_{384}$  should have 32  $\text{Na}^+$  ions at site III' and should be able to accept 16  $\text{Na}^0$  atoms, filling site V.

This may not be the same  $\text{Na}_3^{2+}$  cluster described by ESR in zeolite Y.<sup>29</sup> The linear  $\text{Na}_3^{2+}$  cluster would not be expected to form as readily in the more silicious forms of zeolite FAU. Zeolite Y has fewer  $\text{Na}^+$  ions, insufficient for any to occupy site III' unless they are "promoted" to form this cluster. Also, the  $\text{Na}^+$  ions and the near  $\text{Na}^0$  atom in each cluster would need to be exchanging rapidly to appear equivalent to ESR; this, however, they should be able to do easily.<sup>20</sup>

This linear  $\text{Na}_3^{2+}$  cluster is quite different from the triangular  $\text{K}_3^{2+}$  cluster of similar stoichiometry identified crystallographically in zeolite A.<sup>5</sup>

A compelling reason for any long-range ordering of these  $\text{Na}_3^{2+}$  clusters was not apparent from an inspection of the structure.

This is only the third sodium cluster whose structure has been determined crystallographically. In the first, the centered tetrahedral  $\text{Na}_5^{4+}$  cluster in zeolite X, the Na–Na bond length is 2.80(2) Å.<sup>12</sup> For the linear  $\text{Na}_3^{2+}$  cluster, the corresponding distance is 2.93(4) Å. Both of these values agree with the sum of the radii of  $\text{Na}^+$  and  $\text{Na}^0$ ,  $0.97 + 1.86 = 2.83$  Å. Much longer intersodium distances of 4.40(2) Å are found for  $(\text{Na}_4)^{3+}$  in zeolite Y.<sup>6</sup>  $\text{Na}_4^{3+}$  is, however, qualitatively different from the first two clusters because its valence electron density is evenly distributed.  $\text{Na}_5^{4+}$  and  $\text{Na}_3^{2+}$  contain a unique, near neutral, central atom.

The near-colorlessness of this  $\text{Na}_3^{2+}$  cluster can be attributed to the result that its odd electron is minimally delocalized beyond its central atom, which places its absorption in the ultraviolet region. This is consistent with the trend seen in the colors of  $\text{Na}_6^{5+}$  in zeolite Y (blue-black),<sup>30</sup>  $\text{Na}_5^{4+}$  in zeolite X (blue<sup>31</sup> or pink<sup>12</sup>), and  $\text{Na}_4^{3+}$  in zeolite Y (pink-red).<sup>13</sup> The largest cluster,  $\text{Na}_6^{5+}$ , may have the most electron delocalization; its electronic energy levels would then be closer together, allowing it to absorb near the middle of the visible region and to be blue-black. This argument suffers because correspondences between the colors observed and specific clusters are not, in general, firmly established.

In summary, when dehydrated Na-X is exposed to a low pressure of sodium metal vapor, pairs of site-III'  $\text{Na}^+$  ions each capture or accommodate a sodium atom between them to form linear clusters of  $\text{Na}_3^{2+}$ . This reaction proceeds until all site-III'  $\text{Na}^+$  ions have reacted. Site V affords a  $\text{Na}^0$  atom an opportunity to delocalize its valence electron.

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**Supporting Information Available:** Table of observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

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