

# Crystal Structure of a Benzene Sorption Complex of Dehydrated Fully Ca<sup>2+</sup>-Exchanged Zeolite X

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Received: March 10, 1998; In Final Form: May 18, 1998

The crystal structure of a benzene sorption complex of fully dehydrated Ca<sup>2+</sup>-exchanged zeolite X, Ca<sub>46</sub>Si<sub>100</sub>Al<sub>92</sub>O<sub>384</sub>·28C<sub>6</sub>H<sub>6</sub> ( $a = 24.953(6)$  Å), has been determined by single-crystal X-ray diffraction techniques in the cubic space group  $Fd\bar{3}$  at 21 °C. The crystal was prepared by ion exchange in a flowing stream of 0.05 M aqueous Ca(NO<sub>3</sub>)<sub>2</sub> for 3 days, followed by dehydration at 400 °C and  $2 \times 10^{-6}$  Torr for 2 days, followed by exposure to about 48 Torr of benzene vapor at 16 °C. The structure was determined in this atmosphere and refined to the final error indices  $R_1 = 0.051$  and  $R_w = 0.049$  with 358 reflections for which  $I > 3\sigma(I)$ . Filling site I (at the centers of the double six-rings), 16 octahedrally coordinated Ca<sup>2+</sup> ions (Ca–O = 2.399(7) Å) are found per unit cell. The remaining 30 Ca<sup>2+</sup> ions are found at two nonequivalent sites II (in the supercages) with occupancies of 8 and 22 ions. Each of these Ca<sup>2+</sup> ions coordinates to three framework oxygens, either at 2.270(10) or 2.318(7) Å, respectively, and extends either 0.24 or 0.55 Å, respectively, into the supercage from the plane of the three oxygens to which it is bound. The benzene molecules are found at two distinct sites within the supercages. Twenty-two benzenes lie on 3-fold axes in the large cavities, where they interact facially with the latter 22 site-II Ca<sup>2+</sup> ions (Ca<sup>2+</sup>–benzene center = 2.75 Å; occupancy = 22 molecules/32 sites). The remaining six benzene molecules are found in 12-ring planes; occupancy = 6 molecules/16 sites. Each hydrogen of these six benzenes is ca. 3.0 Å from three 12-ring oxygens.

## Introduction

The sorption of aromatic molecules by zeolites has been the subject of much research because of the utility of zeolites as molecular sieves and catalysts. To understand the catalytic behavior of zeolites, knowledge is required not only of the distribution of the cations but also of the interactions between the cations and the sorbed molecules, between the framework and the sorbed molecules, and among the sorbed molecules themselves.

The structure of zeolite Na-X, which is isomorphous with the mineral faujasite, is well established by X-ray diffraction.<sup>1,2</sup> The system of benzene sorbed on synthetic faujasite-type zeolite has drawn significant attention in recent years. For instance, Cheetham et al.<sup>3</sup> determined the crystal structure of Na-X (Si/Al = 1.21) and that of its complex with benzene at 5 K by Rietveld analysis of powder neutron-diffraction data. In the latter structure, ca. 0.32 benzene molecule per supercage associates with site-II cations. No benzene was found in 12-rings. The same work was done with zeolite Na-Y by Fitch et al.;<sup>4,5</sup> at room temperature, the benzene molecules appeared to be largely delocalized within the supercages of Na-Y, but at 4 K they are found at two distinct sites, one centered in the plane of a 12-ring and the other opposite a six-ring, both with their planes perpendicular to 3-fold axes. Studies at room temperature

by small-angle neutron scattering of Na-Y with sorbed benzene suggested that, at a benzene coverage of 2.5 molecules per supercage, there is a tendency for the benzene molecules to aggregate in a limited number of cavities. At the low coverage of 1.0 molecule per supercage, a more even distribution of benzene molecules is observed.<sup>6</sup> Using high-speed X-ray powder diffraction methods, the influence of temperature on the sorption of benzene in K<sup>+</sup>-, Ca<sup>2+</sup>-, and Sr<sup>2+</sup>-exchanged Y-type zeolites was investigated;<sup>7</sup> the ability of benzene to alter the cation distribution increases rapidly with the cation–benzene interaction energy.

Low-temperature NMR investigations indicate that the benzene molecule is rapidly rotating in its plane while coordinating to the site-II cation.<sup>8</sup> The stability of this site is believed to be due primarily to an electrostatic quadrupolar rather than to a  $\pi$ -type interaction; these benzene molecules are further stabilized by electrostatic interactions between the benzene hydrogens and the zeolite framework. A second sorption site in Na-Y was identified at the center of the 12-ring window; this occurred at higher concentrations of benzene in Na-Y (2.6 molecules per supercage) and also when different cations are exchanged for sodium. The sorption of benzene on dehydrated Na-Y has also been studied by <sup>129</sup>Xe, proton, and <sup>13</sup>C NMR.<sup>9</sup> The maximum number of benzene molecules that can be sorbed within a zeolite supercage was found to lie between 4.9 and 5.2. The nature of

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

atom	wyc. pos.	site	x	y	z	$U_{11}^b$ or $U_{iso}^d$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$	occupancy	
												varied	fixed
Si	96(g)		-542(1)	1231(2)	334(1)	141(15)	116(15)	84(15)	-24(18)	-16(16)	-8(19)		96.0
Al	96(g)		-562(1)	369(1)	1217(2)	121(16)	94(16)	77(16)	-3(16)	11(19)	-16(20)		96.0
O(1)	96(g)		-1128(3)	15(3)	1069(3)	114(5)	235(48)	135(46)	35(42)	-25(33)	14(40)		96.0
O(2)	96(g)		-36(4)	-38(3)	1431(3)	226(44)	72(40)	172(45)	83(38)	-14(40)	-43(38)		96.0
O(3)	96(g)		-360(3)	657(3)	603(3)	235(47)	20(41)	127(43)	21(42)	5(41)	-77(34)		96.0
O(4)	96(g)		-614(3)	801(3)	1735(3)	320(51)	104(42)	120(44)	-78(45)	45(47)	-30(37)		96.0
Ca(1)	16(c)	I	0	0	0	140(15)	140(15)	140(15)	7(17)	7(17)	7(17)	15.7(2)	16.0
Ca(2)	32(e)	II(a)	2224(10)	2224(10)	2224(10)	1260(95)	1260(95)	1260(95)	913(115)	913(115)	913(115)	7.3(3)	8.0
Ca(3)	32(e)	II(b)	2295(2)	2295(2)	2295(2)	216(17)	216(17)	216(17)	66(20)	66(20)	66(20)	21.9(3)	22.0
C(1)	96(g)		2515(12)	3338(11)	2938(11)	873(105)						60(2)	66.0
C(2)	96(g)		2522(15)	2936(13)	3358(13)	1234(138)						71(3)	66.0
C(3)	96(g)		4754(32)	4683(28)	5366(24)	1241(288) <sup>e</sup>						37(2)	36.0
H(1) <sup>f</sup>	96(g)		2194	3624	2934 <sup>f</sup>								66.0
H(2) <sup>f</sup>	96(g)		2229	2943	3679 <sup>f</sup>								66.0
H(3) <sup>f</sup>	96(g)		4593	4593	5813 <sup>f</sup>								36.0

<sup>a</sup> Positional and thermal parameters are given  $\times 10^4$ . 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 =  $\exp[(-2\pi^2/a^2)(h^2U_{11} + k^2U_{22} + l^2U_{33} + 2hkU_{12} + 2hlU_{13} + 2klU_{23})]$ . <sup>c</sup> Occupancy factors are given as the number of atoms or ions per unit cell. <sup>d</sup>  $U_{iso} = B_{iso}/8\pi^2$ . <sup>e</sup> To show a planar benzene molecule, the relationship<sup>4</sup>  $2x + z = 1.5$  is used to obtain the revised C(3) coordinates of (0.4771, 0.4771, 0.5481). Least-squares refinement with the C(3) fixed at (0.4771, 0.4771, 0.5481) raised the *R* indices by 0.001. The *x* coordinate of C(3) deviates by less than  $1\sigma$ , and *y* and *z* by less than  $4\sigma$ , from the revised coordinates of C(3). <sup>f</sup> These hydrogen coordinates were calculated using the best-plane coordinates for benzene(1) and benzene(2).

the sorption sites and the mobility of benzene in Na-Y zeolite around room temperature were investigated by using molecular dynamics calculations carried out at a loading of two molecules per supercage.<sup>10</sup> In that work, benzene molecules were found near six-rings and in 12-rings and could be seen to migrate from one site to another. Pearson et al.<sup>11</sup> used multiple-quantum NMR to measure the apparent spin network size as a function of excitation time for Na-Y containing varying amounts of benzene. They found a uniform distribution of benzene molecules among the supercages at high concentrations of benzene. The site-hopping dynamics of benzene on Ca-LSX have been studied by solid-state exchange <sup>13</sup>C NMR.<sup>12</sup>

The diffusion coefficient and activation energy of benzene in siliceous faujasite have been determined from <sup>2</sup>H NMR measurements and molecular dynamics calculations.<sup>13</sup> Unlike Na-Y, where benzene binds to site-II cations, no specific sorption site is observed in the siliceous analogue; this is reflected in significantly higher diffusion coefficients and a lower activation energy. On the 25 ps time scale of the MD simulation, the behavior of benzene is largely dominated by intracavity rather than intercavity motion.

The structure of perdeuterated benzene sorbed in zeolite H-SAPO-37 has been studied by powder neutron diffraction and <sup>2</sup>H NMR.<sup>14</sup> The diffraction measurements reveal that benzene is located both above the six-ring and in the plane of the 12-ring window at 5 K. Using <sup>2</sup>H NMR, Cheetham et al.<sup>15</sup> found that C<sub>6</sub>D<sub>6</sub> sorbed in Ca-X (one molecule per supercage) is bound strongly at site II and interacts facially with calcium so that rapid rotation about the 6-fold axis of the sorbate is observed in the temperature range 260–330 K. The structures of Yb,Na-Y zeolites containing sorbed perdeuterated xylenes have been studied at two different xylene coverages at 5 K by powder neutron diffraction. The molecules are located in the supercage; the plane of the aromatic ring is perpendicular to the 3-fold axis, and short contacts to the Na<sup>+</sup> ions at site II' are seen.<sup>16,17</sup>

This work was done to locate the sorbed C<sub>6</sub>H<sub>6</sub> molecules by single-crystal diffraction methods at ambient temperature, to determine the cation shifts upon sorption, and to observe cation–sorbate interactions.

## Experimental Section

**Crystal Preparation.** Large single crystals of zeolite Na-X, stoichiometry Na<sub>92</sub>Si<sub>100</sub>Al<sub>92</sub>O<sub>384</sub>, were prepared in St. Petersburg, Russia.<sup>18</sup> One of these, a colorless octahedron about 0.20 mm in cross section, was lodged in a fine Pyrex capillary. Aqueous 0.05 M Ca(NO<sub>3</sub>)<sub>2</sub> was allowed to flow past the crystal at a velocity of 1.0 cm/s for 3 days. The capillary containing the crystal was attached to a vacuum system, and the crystal was cautiously dehydrated by gradually increasing its temperature (ca. 25 °C/h) to 400 °C at a constant pressure of  $2 \times 10^{-6}$  Torr. Finally, the system was maintained at this state for 48 h. After cooling to room temperature, the crystal remained colorless. To prepare the benzene complex, the crystal was treated with ca. 48 Torr of zeolitically dried benzene for 3 days at 16(1) °C. The resulting colorless crystal, still in its benzene atmosphere, was sealed in its capillary by torch.

**X-ray Data Collection.** The cubic space group  $Fd\bar{3}$  was used. This choice is supported by (a) the low Si/Al ratio, which in turn requires, at least in the short range, alternation 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. Molybdenum  $K\alpha$  radiation was used for all experiments ( $K\alpha_1$ ,  $\lambda = 0.70930$  Å;  $K\alpha_2$ ,  $\lambda = 0.71359$  Å). The unit cell constant at 21(1) °C, determined by least-squares refinement of 25 intense reflections for which  $14^\circ < 2\theta < 22^\circ$ , is  $a = 24.953(6)$  Å. All unique reflections in the positive octant of an *F*-centered unit cell for which  $2\theta < 50^\circ$ ,  $l > h$ , and  $k > h$  were recorded at 21 °C. Of the 1386 unique reflections examined, only the 358 reflections for which  $l > 3\sigma(l)$  were used in subsequent structure determination and refinement. An absorption correction ( $\mu = 0.79$  mm<sup>-1</sup>,  $\rho_{cal} = 1.697$  g/cm<sup>3</sup>, and  $F(000) = 7764$ ) was made empirically using a  $\psi$  scan. The adjusted transmission coefficients ranged from 0.991 to 0.998. These corrections had little effect on the final *R* indices. Other details are the same as previously reported.<sup>19</sup>

## Structure Determination

Full-matrix least-squares refinement was initiated with the atomic parameters of the framework atoms [Si, Al, O(1), O(2),

**TABLE 2: Selected Interatomic Distances (Å) and Angles (deg)<sup>a</sup> for Framework Atoms and Calcium Ions**

Si—O(1)	1.599(8)	O(1)—Si—O(2)	111.9(5)
Si—O(2)	1.638(9) <sup>b</sup>	O(1)—Si—O(3)	107.9(4)
Si—O(3)	1.645(9) <sup>b</sup>	O(1)—Si—O(4)	113.1(5)
Si—O(4)	1.597(9)	O(2)—Si—O(3)	106.5(4)
mean	1.620	O(2)—Si—O(4)	104.1(4)
		O(3)—Si—O(4)	113.2(4)
Al—O(1)	1.706(8)		
Al—O(2)	1.743(9) <sup>b</sup>	O(1)—Al—O(2)	112.8(4)
Al—O(3)	1.767(9) <sup>b</sup>	O(1)—Al—O(3)	104.9(4)
Al—O(4)	1.688(9)	O(1)—Al—O(4)	115.6(4)
mean	1.726	O(2)—Al—O(3)	108.8(4)
		O(2)—Al—O(4)	101.3(4)
Ca(1)—O(3)	2.399(7)	O(3)—Al—O(4)	115.2(4)
Ca(2)—O(2)	2.266(11)	Si—O(1)—Al	126.4(5)
Ca(3)—O(2)	2.318(7)	Si—O(2)—Al	141.1(5)
		Si—O(3)—Al	129.0(5)
		Si—O(4)—Al	166.8(6)
		O(3)—Ca(1)—O(3)	93.6(2)/86.4(2)
		O(2)—Ca(2)—O(2)	118.9(7)
		O(2)—Ca(3)—O(2)	114.6(3)

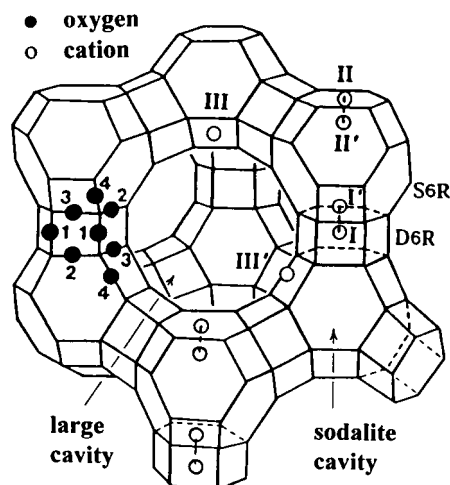
O(3), and O(4)] in dehydrated Ca<sub>46</sub>-X.<sup>20</sup> Isotropic refinement of the framework atoms converged to an unweighted  $R_1$  index,  $(\sum(F_o - |F_c|)/\sum F_o)$ , of 0.28 and a weighted  $R_w$  index,  $(\sum w(F_o - |F_c|)^2/\sum w F_o^2)^{1/2}$ , of 0.34.

A difference Fourier function showed the positions of the Ca<sup>2+</sup> ions at Ca(1), (0.0, 0.0, 0.0) with peak height 14.7 e Å<sup>-3</sup> and at Ca(3), (0.233, 0.233, 0.233) with peak height 9.2 e Å<sup>-3</sup>. Anisotropic refinement of the framework atoms, Ca(1), and Ca(3) converged to  $R_1 = 0.081$  and  $R_w = 0.101$ .

A subsequent difference Fourier synthesis indicated with a peak of height 1.5 e Å<sup>-3</sup> that carbon atoms are at the general position (0.255, 0.328, 0.288). Least-squares refinement including this peak at C(1) with an isotropic temperature factor converged to  $R_1 = 0.073$  and  $R_w = 0.079$ . A subsequent difference Fourier synthesis indicated with a peak of height 1.2 e Å<sup>-3</sup> that the remaining carbon atoms of these benzene molecules are at the general position (0.256, 0.294, 0.333). Least-squares refinement including this peak, C(2), isotropically, converged to  $R_1 = 0.065$  and  $R_w = 0.070$ . A later difference Fourier synthesis indicated with a peak of height 1.0 e Å<sup>-3</sup> that carbon atoms of a second kind of benzene molecule are at the general position (0.486, 0.476, 0.541), C(3). Least-squares refinement including this peak isotropically converged to  $R_1 = 0.058$  and  $R_w = 0.054$ . The thermal ellipsoid of Ca(2) became elongated in subsequent refinements, indicating the presence of two nonequivalent Ca<sup>2+</sup> ions at this position. This position was split into Ca(2) at (0.22, 0.22, 0.22) and Ca(3) at (0.23, 0.23, 0.23). Anisotropic refinement of all atoms, except the carbon atoms, which were refined isotropically, converged to  $R_1 = 0.049$  and  $R_w = 0.045$ .

The occupancy numbers at Ca(1), Ca(2), Ca(3), C(1), C(2), and C(3) were fixed as shown in Table 1 by the assumption of stoichiometry, the requirement of neutrality, and the observation that the occupancies at Ca(3), C(1), and C(2) were refining in the ratios of 1:3:3. All shifts in the final cycles of least-squares refinement were less than 0.01% of their corresponding standard deviations. The final error indices converged to  $R_1 = 0.049$  and  $R_w = 0.045$ . The goodness-of-fit =  $(\sum w(F_o - |F_c|)^2/(m - s))^{1/2} = 1.78$ , where  $m$  (358) is the number of observations and  $s$  (75) is the number of variables in least-squares refinement. The final difference Fourier function was featureless.

Atomic scattering factors<sup>21</sup> for Si, Al, O<sup>-</sup>, C, and Ca<sup>2+</sup> were used. All scattering factors were modified to account for anomalous dispersion.<sup>22</sup> The final structural parameters and



**Figure 1.** Stylized drawing of the framework structure of zeolite X. Near the center of each line segment is an oxygen atom. The different oxygen atoms are indicated by the numbers 1–4. Silicon and aluminum atoms alternate at the tetrahedral intersections, except that Si substitutes for about four of the Al's per unit cell. Extraframework cation positions are indicated with Roman numerals.

selected interatomic distances and angles are presented in Tables 1 and 2, respectively.

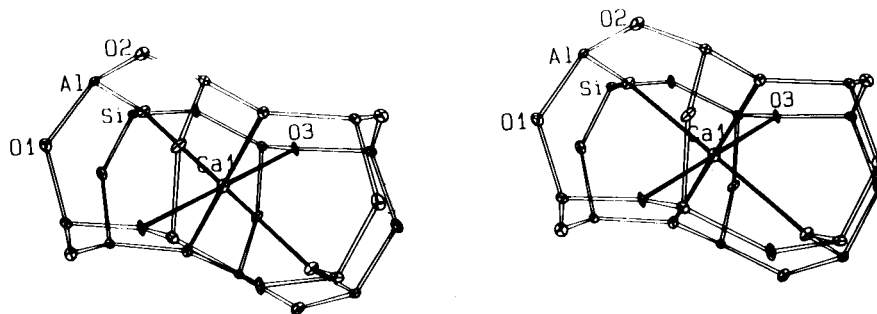
## Discussion

Zeolite X is a synthetic counterpart of the naturally occurring mineral faujasite. The 14-hedron with 24 vertices known as the sodalite cavity or  $\beta$  cage may be viewed as the principal building block of the aluminosilicate framework of the zeolite. These  $\beta$  cages are connected tetrahedrally at six-rings by bridging oxygens, O(1)'s (see Figure 1), 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-ring (24-membered) windows. The Si and Al atoms occupy the vertices of these polyhedra. The oxygen atoms lie approximately halfway 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, I' in the sodalite ( $\beta$ ) 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, shared by a  $\beta$  cage and a supercage) 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).<sup>23,24</sup>

The ordering of the Al and Si atoms in the lattice, justifying the choice of space group  $Fd\bar{3}$ , is confirmed by the average values of the Si—O (1.620 Å) and Al—O (1.726 Å) distances. These averaged bond distances are not sensitive to ion exchange and dehydration. The individual bond lengths, however, show marked variations: Si—O from 1.597(9) to 1.645(9) Å and Al—O from 1.688(9) to 1.767(9) Å (see Table 2). The individual Si—O and Al—O distances depend on Ca<sup>2+</sup> coordination to framework oxygen. O(1) and O(4) are not involved in coordination; Ca<sup>2+</sup> ions at sites I and II coordinate only to O(2) and O(3). Accordingly, the (Si,Al)—O(2) and (Si,Al)—O(3) distances are lengthened (see Table 2). This effect is commonly seen in fully divalent cation-exchanged zeolite X.<sup>20,25</sup>

In Ca<sub>46</sub>-X·28C<sub>6</sub>H<sub>6</sub>, all Ca<sup>2+</sup> ions are found at three different crystallographic sites of high occupancy. The 16 Ca<sup>2+</sup> ions at



**Figure 2.** Stereoview of a double six-ring. The ion at Ca(1) is shown at site I. Ellipsoids of 20% probability are used.

**TABLE 3: Selected Interatomic Distances (Å) and Angles (deg)<sup>a</sup> Involving Sorbed Benzene Molecules**

Benzene(1)		Benzene(2)	
C(1)–C(2)	1.45(4)	C(3)–C(3)	1.41(10) <sup>b</sup>
C(2)–C(1)′	1.48(5)	C(3)–H(3)	1.085
C(1)–H(1)	1.085	C(3)–C(3)′–C(3)″	112(6)/120 <sup>b</sup>
C(2)–H(2)	1.085	Benzene(2)–Framework	
C(1)–C(2)–C(1)′	118(3)	C(3)–O(1)	3.78(6)/3.76(7) <sup>b</sup>
C(2)–C(1)–C(2)′	121(3)	C(3)–O(4)	4.20(6)/4.02(6) <sup>b</sup>
Benzene(1)–Ca(3)		H(3)–O(1)	3.10/3.02 <sup>b</sup>
C(1)–Ca(3)	3.11(3)	H(3)–O(4)	3.18/2.93 <sup>b</sup>
C(2)–Ca(3)	3.14(3)	Benzene(1)–Benzene(1)	
Center <sup>c</sup> –Ca(3)	2.75	C(1)–C(1)′	4.54(4)
Benzene(1)–Framework		C(1)–C(2)′	4.30(4)
C(1)–O(1)	3.85(3)	C(2)–C(2)′	4.52(5)
C(1)–O(2)	3.51(3)	H(1)–H(1)′	4.12
C(1)–O(4)	3.70(3)	H(1)–H(2)′	3.21
C(2)–O(1)	3.67(4)	H(2)–H(2)′	4.07
C(2)–O(2)	3.54(4)	Benzene(1)–Benzene(2)	
C(2)–O(4)	3.68(4)	C(1)–C(3)	3.68(7)/3.44(7) <sup>b</sup>
H(1)–O(1)	3.03	C(2)–C(3)	3.54(7)/3.40(7) <sup>b</sup>
H(1)–O(2)	3.48	H(1)–H(3)	(2.41, 2.82) <sup>b</sup> /(2.31, 3.17) <sup>d</sup>
H(1)–O(4)	3.54	H(2)–H(3)	(2.38, 2.77) <sup>b</sup> /(2.21, 3.40) <sup>d</sup>
H(2)–O(1)	2.94		
H(2)–O(2)	3.60		
H(2)–O(4)	3.56		

<sup>a</sup> Numbers in parentheses are estimated standard deviations in the units of the least significant digit given for the corresponding value. <sup>b</sup> Bond distances and angles for benzene(2)'s best C<sub>6</sub>-ring plane. <sup>c</sup> Center of C<sub>6</sub>H<sub>6</sub>. <sup>d</sup> Some of these contacts may be avoided as these partially occupied benzene positions are filled.

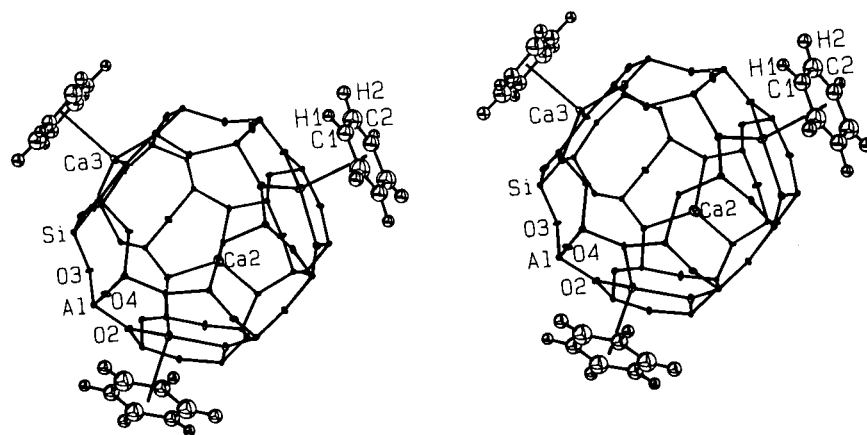
Ca(1) fill site I at the center of the D6R's (see Figure 2). The octahedral Ca(1)–O(3) distance, 2.399(7) Å, is a little longer than the sum of the corresponding ionic radii, 0.99 + 1.32 = 2.31 Å,<sup>26</sup> indicating a reasonably good fit. The eight at Ca(2) and 22 at Ca(3) are located at two sites II in the supercage; each coordinates at 2.266(11) and 2.318(7) Å, respectively, to three O(2) framework oxygens. The O(2)–Ca(2)–O(2) angle is 118.9(7)° and the O(2)–Ca(3)–O(2) angle is 114.6(3)° (see Table 2).

Crystallographically there are two kinds of benzene molecules. The first, benzene(1), is on a 3-fold axis deep inside the supercage with 132 carbon atoms (22 molecules of C<sub>6</sub>H<sub>6</sub>) per unit cell at two sites, C(1) and C(2); these interact facially with the 22 Ca<sup>2+</sup> ions at site II (Ca(3)–benzene center = 2.75 Å) (see Table 3 and Figure 3). Benzene(1) deviates insignificantly from planarity (see Table 4). Even though benzene(1) has relatively high thermal motion, its geometry is close to ideal (C(1)–C(2) = 1.45(4) and C(2)–C(1)′ = 1.48(5) Å; C(1)–C(2)–C(1) = 118(3)° and C(2)–C(1)–C(2) = 121(3)°) (see Table 3 and Figures 3, 4, and 5). The C–C distance in C<sub>6</sub>H<sub>6</sub>(g) is 1.397(1) Å.<sup>27</sup> The positions of the hydrogen atoms, H(1) and H(2), were calculated by the computer system MolEN<sup>28</sup> using C–H = 1.085 Å.

The coordination of benzene(1) has caused Ca(3) to move ca. 0.25 Å along its 3-fold axis more deeply into the supercage

from the three O(2) plane (see Figure 3 and Table 5), compared to its position in dehydrated Ca<sub>46</sub>-X.<sup>20</sup> In this small way, these Ca<sup>2+</sup> ions are able to coordinate more octahedrally to benzene(1) (considering benzene to be tridentate). The deviation of these Ca<sup>2+</sup> ions from the six-ring plane at O(2) into the supercage is larger than those in Ca<sub>46</sub>-X·30C<sub>2</sub>H<sub>2</sub><sup>29</sup> and Ca<sub>46</sub>-X·30C<sub>2</sub>H<sub>4</sub>,<sup>29</sup> and smaller than that in Ca<sub>46</sub>-X·138H<sub>2</sub>S<sup>30</sup> (see Table 5). This and the Ca(3)–O(2) bond distances (see Table 5) suggest that, in binding to the benzene(1) molecule, the interaction between Ca(3) and the O(2) framework oxygens is slightly reduced. The benzene(1) site is considerably less than fully occupied (22/32), and 22 of the 30 Ca<sup>2+</sup> ions at the sites II bind to benzene(1). The eight Ca<sup>2+</sup> ions at Ca(2) which do not coordinate to benzene(1) are recessed only 0.24(1) Å into the supercage from their O(2) plane; compared to dehydrated Ca<sub>46</sub>-X,<sup>20</sup> each of these Ca<sup>2+</sup> ions deviates 0.06 Å less from the plane of its three O(2) oxygens, to which it coordinates more trigonally. Three-coordinate Ca<sup>2+</sup> has remarkably high thermal motion at this position: this had been seen before crystallographically<sup>31</sup> and is well established by molecular dynamics calculations.<sup>32</sup>

The closest approach between benzene(1) and the zeolite framework involves the H(2) hydrogen atom and O(1) at a distance 2.94 Å, suggestive of a very weak electrostatic

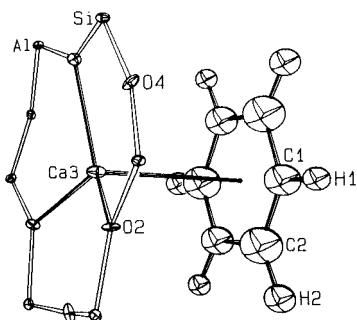


**Figure 3.** Stereoview of a sodalite cavity. Three  $\text{Ca}^{2+}$  ions are shown at Ca(3). Each coordinates to a benzene molecule. The  $\text{Ca}^{2+}$  ion at Ca(2) does not coordinate to benzene. Ellipsoids of 20% probability are used.

**TABLE 4: Deviations of Atoms ( $\text{\AA}$ ) from (111) Planes**

	position	site	displacement
at O(2) <sup>a</sup>	Ca(2)	II(a)	0.24(1)
	Ca(3)	II(b)	0.55(1)
	C(1)		3.29(3)
	C(2)		3.32(3)
at O(3) <sup>b</sup>	Ca(1)	I	1.29(1)
	C(1)		-0.02(3)
at benzene(1)	C(2)		+0.02(3)
at benzene(2)	C(3)		+0.23(6), -0.23(6)

<sup>a</sup> A positive displacement indicates that the ion or atom lies in the supercage. <sup>b</sup> The positive displacement indicates that the ion lies within a double six-ring.



**Figure 4.**  $\text{Ca}(\text{C}_6\text{H}_6)^{2+}$  complex on the inner surface of a supercage. Ellipsoids of 20% probability are used. Twenty-two  $\text{Ca}^{2+}$  ions at Ca(3) coordinate to benzene molecules as shown.

interaction. The smallest distance between adjacent benzene(1) molecules is between hydrogen atoms,  $\text{H}(1)-\text{H}(2)' = 3.21 \text{ \AA}$ .

The benzene(1) sorption site is similar to those observed in Na-Y<sup>4</sup> at a loading level of 2.6 molecules per supercage and in Ca-X<sup>15</sup> with one molecule per supercage. Cheetham et al.,<sup>15</sup> by studying Ca-X with sorbed  $\text{C}_6\text{D}_6$  by <sup>2</sup>H NMR, confirmed that deuterated benzene is bound strongly at site II and that it interacts facially with calcium so that rapid rotation about the 6-fold axis of the sorbate is observed in the temperature range 260-330 K. The activation energy for this rotation is 4.9 kJ mol<sup>-1</sup>. The precise nature of the cation-benzene interaction is unclear, but charge-quadrupolar terms are believed to be important.<sup>33</sup> The stability of this site is believed to be due more to a quadrupolar than to a  $\pi$ -type interaction.

The second kind of benzene molecule (six per unit cell) lies in the best plane of the 12-ring and is at its center. Benzene(2) has symmetry  $\bar{3}$ , so it can be generated crystallographically from a single carbon position ( $\text{C}(3)-\text{C}(3) = 1.41(1) \text{ \AA}$  and  $\text{C}(3)-$

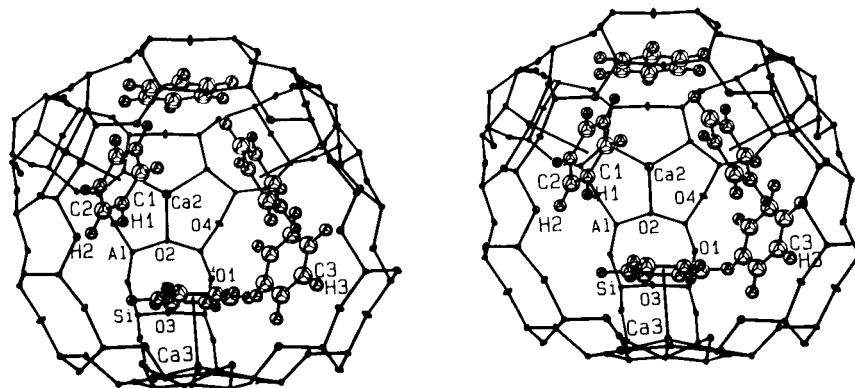
$\text{C}(3)-\text{C}(3) = 112(6)^\circ$ ). There are strong interactions between the hydrogens of benzene(2) and the oxygens of the 12-ring window. Figure 6 is a van der Waals drawing of a benzene(2) molecule in a 12-ring (which is not a planar ring). The benzene(2) molecule found crystallographically is unrealistically puckered (see Table 4 and Figure 6); this puckering is not crystallographically significant.

Benzene usually occupies 12-rings only at high loadings.<sup>4,10</sup> The observation of simultaneous occupation at the six- and in the 12-ring sites is in excellent agreement with previous neutron diffraction results.<sup>4</sup> The 12 oxygen atoms of a 12-ring provide a remarkably close-fitting environment for the benzene molecule; weak but multiple van der Waals forces and electrostatic forces (each H atom approaches three framework oxygens) are likely to be involved.

The six O(4) atoms of each 12-ring (symmetry  $\bar{3}$ ) are alternately 0.46  $\text{\AA}$  above and 0.46  $\text{\AA}$  below the best 12-ring plane, which is also the best benzene(2) plane (see Figure 6). Fitch et al.<sup>4</sup> suggested that this distance decreases a little with increasing benzene content: 0.56  $\text{\AA}$  in empty zeolite Na-Y and 0.54  $\text{\AA}$  at low coverage. This effect is not seen here: the 0.46  $\text{\AA}$  distance in the complex differs insignificantly from that in empty Ca<sub>46</sub>-X, 0.47  $\text{\AA}$ .<sup>19</sup> The distance from the center of the window to O(1) is 4.95  $\text{\AA}$  in Ca<sub>46</sub>-X·28C<sub>6</sub>H<sub>6</sub> and 4.96  $\text{\AA}$  in Ca<sub>46</sub>-X, indicating that benzene sorption has little effect on the framework geometry. However, Fitch et al.<sup>4</sup> found that the distance from the center of the window to the O(1) atoms decreases from 5.06  $\text{\AA}$  in the bare and low-coverage samples to 5.01  $\text{\AA}$  at high coverage in their powder neutron-diffraction studies of the sorption of benzene in Na-Y at 4 K.

From Table 3, the 3.40(7)  $\text{\AA}$  C...C distance between the benzene(1) and benzene(2) molecules is less than the shortest C...C distance among the benzene(1) molecules themselves, 4.30(4)  $\text{\AA}$ . Correspondingly, the distances between H(3) of the best-plane benzene(2) molecule and H(1) and H(2) of benzene(1) are  $\text{H}(3)-\text{H}(1) = 2.41$  and  $2.82 \text{ \AA}$  and  $\text{H}(3)-\text{H}(2) = 2.38$  and  $2.77 \text{ \AA}$  (see Table 3). The shortest of the above distances may be avoided by the placement of the benzene molecules in their positions of partial occupancy. The benzene molecules are therefore crowded in this complex, providing a structural basis for the observed sorption limit under the conditions employed.

From the <sup>129</sup>Xe, proton, and <sup>13</sup>C NMR studies,<sup>9</sup> the maximum number of benzene molecules that can occupy each Na-Y supercage is between 4.9 and 5.2. Pearson et al.<sup>11</sup> found that guest molecules appear to sorb randomly at available cationic sites II at loadings of less than three molecules per supercage.

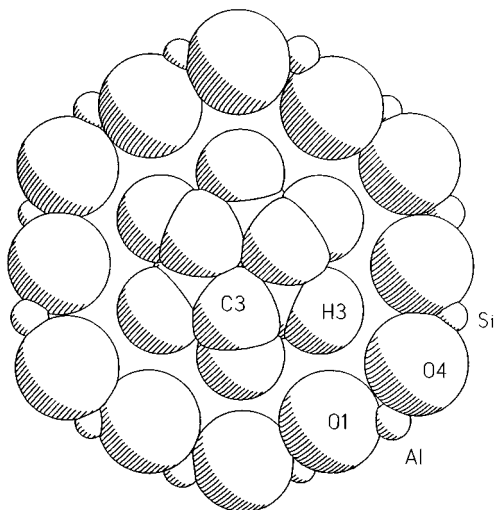


**Figure 5.** Stereoview of a supercage. Three  $\text{Ca}^{2+}$  ions at Ca(3) are shown. Each coordinates to a benzene(1) molecule. The  $\text{Ca}^{2+}$  ion at Ca(2) does not coordinate to benzene. Two benzene(2) molecules are shown at 12-ring centers. Ellipsoids of 20% probability are used.

**TABLE 5: Structural Features of  $\text{Ca}_{46}\text{-X}$  and Its Sorption Complexes**

	dehydrated	$\cdot 30\text{C}_2\text{H}_2$	$\cdot 30\text{C}_2\text{H}_4$	$\cdot 28\text{C}_6\text{H}_6$	$\cdot 138\text{H}_2\text{S}$
number of $\text{Ca}^{2+}$ ions at site I	16	16	16	16	16
number of $\text{Ca}^{2+}$ ions at site II	30	30	30	8, 22	30
frac. coord. of $\text{Ca}^{2+}$ at site II (or II(a), II(b))	0.2234	0.2265	0.2264	0.2224, 0.2295	0.2372
deviation of $\text{Ca}^{2+}$ from the six-ring plane at O(2) ( $\text{\AA}$ ) <sup>a</sup>	0.30	0.42	0.41	0.24, 0.55	0.83
$\text{Ca}^{2+}\text{-O}(2)$ ( $\text{\AA}$ )	2.276	2.318	2.316	2.266, 2.318	2.37
$\text{O}(2)\text{-Ca-O}(2)$ (deg)	118.3	116.8	117.0	118.9, 114.6	108.3
reference	20	29	29	this work	30

<sup>a</sup> A positive deviation indicates that the ion lies in the supercage.



**Figure 6.** Van der Waals view of a 12-ring containing a benzene(2) molecule. Six of the 16 12-rings per unit cell are so occupied. The van der Waals radii used for oxygen and hydrogen are 1.40 and 1.20  $\text{\AA}$ , respectively. The positions plotted are those found crystallographically except for those of the hydrogen atoms: the H(3) coordinates were calculated from the best-plane benzene(2) molecule. Note that each H(3) atom is near one O(4) and two O(1) framework oxygens; altogether then each benzene(2) molecule has 18 such  $\text{H}\cdots\text{O}$  interactions. The fit is remarkable. The view is along (111); the center is at (0.5, 0.5, 0.5); the symmetry is  $\bar{3}$ .

The distribution becomes uniform as the loading approaches three benzene molecules per supercage.

The C(1)–C(3) and C(2)–C(3) distances of 3.44 and 3.40  $\text{\AA}$ , respectively, indicate that clusters of benzene molecules may have formed within the supercages. A small angle neutron scattering study<sup>6</sup> indicates that when one molecule is sorbed per supercage, it remains fixed on cationic sites and is ordered in the network. When larger amounts are sorbed, a general tendency is seen for the molecules to segregate in a limited number of supercages to form 10–20  $\text{\AA}$  clusters.

In summary,  $\text{Ca}^{2+}$  ions occupy sites I and II: 16 per unit cell at site I and 30 at site II. There are two kinds of site-II  $\text{Ca}^{2+}$  ions: 22 coordinate to benzene molecules; eight do not. There are two kinds of benzene molecules: 22 coordinate to six-ring  $\text{Ca}^{2+}$  ions in the supercage; six fit remarkably well in 12-ring windows.

**Acknowledgment.** This work was supported in part by the Basic Research Institute Program, Ministry of Education, Korea, 1997, Project No. BSRI-97-3409. Mr. Shenyan Zhen produced Figure 6.

**Supporting Information Available:** Tables of observed and calculated structure factors with esd's (7 pages). Ordering information is given on any current masthead page.

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