

Crystal Structure of a Mesitylene Sorption Complex of Dehydrated Fully Ca^{2+} -Exchanged Zeolite X. Sorbed Mesitylene Appears to be Significantly Nonplanar

Eun Young Choi,[†] Yang Kim,^{*,†} and Karl Seff^{*,‡}

Department of Chemistry and Chemistry Institute for Functional Materials, Pusan National University, Pusan 609-735, Korea, and Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822

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The crystal structure of a mesitylene sorption complex of fully dehydrated Ca^{2+} -exchanged zeolite X, $\text{Ca}_{46}\text{Si}_{100}\text{Al}_{92}\text{O}_{384}\cdot 8\text{C}_9\text{H}_{12}$ ($a = 24.966(4)$ 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 $\text{Ca}(\text{NO}_3)_2$ for 4 d, followed by dehydration at 400 °C and 2×10^{-6} Torr for 2 d (colorless) and then exposure to ca. 2.1 Torr of zeolitically dry mesitylene vapor at 20 °C. The structure of the resulting dark-brown crystal was determined in this atmosphere and was refined to the final error index $R_1 = 0.046$ with 253 reflections for which $F_o > 4\sigma(F_o)$; wR_2 based on F^2 and all data (1153) is 0.128. In this structure, 16 Ca^{2+} ions fill site I (at the centers of the double 6-rings), and the remaining 30 Ca^{2+} ions are found at two nonequivalent sites II (near 6-rings in the supercages) with occupancies of 22 and 8 ions. Each of these Ca^{2+} ions coordinates to three framework oxygens and extends 0.262 or 0.584 Å, respectively, into the supercage from the plane of the three oxygens to which it is bound. One mesitylene molecule per supercage lies on a 3-fold axis where it interacts facially with one of the latter eight Ca^{2+} ions (Ca^{2+} –mesitylene center = 2.70 Å). All three hydrogen atoms of the central ring and one hydrogen atom of each methyl group are near framework oxygens. (Hydrogen atom positions were calculated from carbon positions.) Altogether, each mesitylene molecule has six close $\text{H}\cdots\text{O}$ interactions with zeolite oxygens: three ring $\text{H}\cdots\text{O} = 2.70$ Å and three methyl $\text{H}\cdots\text{O} = 2.52$ Å. Mesitylene appears to be distorted in the same way and to a similar extent as half of the strained molecule [2.2.2](1,3,5)cyclophane-1,9,17-triene.

Introduction

Because of their high internal surface areas and molecularly sized cages and windows, zeolites are extensively used as shape-selective catalysts and adsorbents in a variety of reactions and separation processes.^{1,2} Heterogeneous catalytic processes are facilitated by the physical and electronic distortions that zeolites impose on molecules at sorption sites.

Hydrocarbons sorbed into zeolites have been investigated extensively by a variety of techniques, especially X-ray diffraction,³ neutron diffraction,⁴ and infrared spectroscopy.⁵ These investigations have provided detailed information about the sorption sites selected by organic guest species and their distribution among those sites. In addition, the inaccessibility of some sites to some molecules can be seen.

Much of the single-crystal X-ray diffraction work is summarized in a recent review article.⁶ Included there are C_2H_2 ,^{7,8} C_2H_4 ,^{7,9,10} C_3H_6 ,^{11,12} and C_6H_6 .^{13,14} Using high-speed X-ray powder-diffraction methods, the influence of temperature on the sorption of benzene in K^+ -, Ca^{2+} -, and Sr^{2+} -exchanged zeolite Y was investigated.¹⁵ The sorption of PhMe, *m*-xylene, mesitylene, PhCMe₃, and PhCH₂OH on Na–Y, H,Na–Y, Mg,H,Na–Y, and Co,H,Na–Y zeolites was studied by IR.¹⁶ The sorption of benzene by faujasite zeolites was repeatedly investigated by a variety of spectroscopic techniques, including UV,^{17,18} IR,^{19–21} and Raman.²² High-resolution powder neutron-diffraction studies have already been successful in locating a

number of hydrocarbon molecules in zeolites, such as benzene,²³ *o*-, *m*-, and *p*-xylene,²⁴ pyridine,²⁵ and aniline²⁶ in zeolite Y and benzene²⁷ and pyridine²⁸ in zeolite L. 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. These perdeuterated xylene molecules were found in the supercages; the planes of their aromatic rings are perpendicular to 3-fold axes, and short contacts to Na^+ ions at site II are seen.^{24,29}

The placements of benzene molecules sorbed by sodium zeolite Y has been observed by powder diffraction.^{23,30} At room temperature, the benzene molecules are “largely delocalized within the supercages” of zeolite Y,²³ whereas at 4 K, the benzene molecules are found at two distinct 3-fold axis sites: one is near site II, and the other is at the center of the 12-ring windows between adjacent supercages.²³ Benzene molecules were found at the same two sites at 21 °C in the structure of Ca–X highly loaded with benzene, $\text{Ca}_{46}\text{X}\cdot 28\text{C}_6\text{H}_6$, determined by single-crystal X-ray diffraction.¹³ Powder neutron-diffraction studies in the temperature range 260–330 K have revealed that C_6D_6 sorbed in Ca–X (one molecule per supercage) is bound strongly at site II, where it interacts facially with Ca^{2+} .³¹ Low-temperature NMR investigations indicate that the benzene molecule is rapidly rotating in its plane while coordinating to the site II cation.³² The stability of this site is attributed primarily to an electrostatic quadrupolar interaction with π polarization and van der Waals forces also contributing to the bonding;³³ these benzene molecules are further stabilized by electrostatic interactions between the benzene hydrogens and the zeolite framework.

* Corresponding authors. E-mail: ykim@pusan.ac.kr; seff@hawaii.edu.

[†] Pusan National University.

[‡] University of Hawaii.

Mesitylene (1,3,5-trimethylbenzene, TMB) is a neurotoxic compound.³⁴ It is a component of numerous commercial preparations of organic solvents used in the chemical, plastics, and printing industries as well as in other industries.³⁴ The toxicity and the biological monitoring of mesitylene has been investigated in the field of environmental chemistry.

Choudhary and Singh³⁵ studied the sorption capacity of zeolite H-ZSM-5 (H-MFI) for different sorbates. In increasing order, the capacities are methane \gg *n*-hexane $>$ *p*-xylene $>$ *m*-xylene \approx *o*-xylene $>$ mesitylene. In unpublished work, a reviewer of this report found no uptake of mesitylene by ZSM-5 using NMR analysis, even after 16 h at 120 °C. The values of the diffusion coefficients for *o*-xylene, *m*-xylene, and mesitylene at 303 K were found to be 24.0×10^{-15} , 16.1×10^{-15} , and 0.9×10^{-15} cm² s⁻¹, respectively.³⁵ Choudhary and Mantri³⁶ studied the interaction of aromatic hydrocarbons (viz. toluene, *p*-xylene, mesitylene, and naphthalene) with sorption sites in purely siliceous MCM-41 zeolite. The heats of sorption of aromatic hydrocarbons onto this mesoporous material, estimated from the TPD (temperature-programmed desorption) peak-maximum temperatures measured at different heating rates, were found to be in the following order: toluene $<$ *p*-xylene $<$ mesitylene $<$ naphthalene.

The distribution of mesitylene in the supercages of Na-Y has recently been studied by ¹²⁹Xe and multiple-quantum NMR.³⁷ The structure of Na,Yb-Y zeolites containing sorbed mesitylene has been studied by powder neutron diffraction at 5 K.³⁸ Mesitylene coordinates to site II Na⁺ ions in the supercage. Two distinct sites II, corresponding to two different positions of the molecules with respect to the framework, are observed. The ring center-Na⁺ ion distances are 2.604(2) and 2.582(2) Å for the molecules in these two positions.

This work was done to locate sorbed mesitylene molecules in Ca₄₆-X by single-crystal diffraction methods at ambient temperature to determine the cation shifts upon sorption and to observe zeolite-sorbate interactions in a dipositive cation form of a zeolite. Such work has been done with benzene,^{13,14} mesitylene is significantly larger.

Experimental Section

Crystal Preparation. Large single crystals of zeolite Na-X, stoichiometry Na₉₂Si₁₀₀Al₉₂O₃₈₄, were prepared in St. Petersburg, Russia.³⁹ 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(NO₃)₂ (pH = 5) was allowed to flow past the crystal at a velocity of 1.0 cm/s for 4 d. (Because of the minor damage that this caused to the crystal, we regret that we did not use a higher pH (vide infra).⁴⁰) 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 2×10^{-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 mesitylene complex, the crystal was treated with ca. 2.1 Torr of zeolitically dried mesitylene for 3 d at 20(1) °C. (The vapor pressure of C₉H₁₂(l) at 20 °C is 2.1 Torr.⁴¹) The resulting dark-brown crystal, still in its mesitylene atmosphere, was flame-sealed in its capillary.

X-ray Data Collection. The cubic space group *Fd* $\bar{3}$ was used. This choice is supported by the low Si/Al ratio, which in turn requires, at least over the short range, the alternation of Si and Al. Mo K α radiation was used for all experiments (K α_1 , λ = 0.70930 Å; K α_2 , λ = 0.71359 Å). The unit cell constant at 21-(1) °C, determined by a least-squares refinement of 25 intense

TABLE 1: Positional,^a Thermal,^a and Occupancy Parameters

atom	Wyc. pos.	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} ^b	occupancy ^c	
						varied	fixed
Si	96(g)	-549(2)	1227(2)	346(2)	113(7)		96
Al	96(g)	-558(2)	358(2)	1212(2)	50(8)		96
O(1)	96(g)	-1118(4)	10(5)	1091(4)	203(28)		96
O(2)	96(g)	-43(4)	-36(4)	1432(3)	121(21)		96
O(3)	96(g)	-357(3)	643(4)	630(4)	107(23)		96
O(4)	96(g)	-599(3)	778(4)	1723(4)	124(22)		96
Ca(1)	16(c)	0	0	0	113(18) ^d	16.7(2)	16
Ca(2)	32(e)	2231(2)	2231(2)	2231(2)	319(27) ^d	21.0(4)	22
Ca(3)	32(e)	2305(5)	2305(5)	2305(5)	127(58)	8.4(8)	8
C(1)	96(g)	3411(60)	2660(61)	2588(69)	824(314)	25.3(24)	24
C(2)	96(g)	3225(89)	2529(82)	3162(80)	1229(450)	25.3(24)	24
C(3)	96(g)	3338(82)	2122(82)	3668(96)	1469(490)	25.3(24)	24
H(1) ^e	96(g)	2454	2342	3617			24
H(3a) ^e	96(g)	3103	2207	3955			24
H(3b) ^e	96(g)	3278	1763	3558			24
H(3c) ^e	96(g)	3699	2161	3784			24

^a Positional and thermal parameters are given $\times 10^4$. Numbers in parentheses are the esds in the units of the least significant digit given for the corresponding parameter. ^b The anisotropic temperature factor = $\exp[-(2\pi^2/a^2)(h^2U_{11} + k^2U_{22} + l^2U_{33} + 2hkU_{12} + 2hlU_{13} + 2klU_{23})]$. ^c Occupancy factors are given as the number of atoms or ions per unit cell. ^d A *U*_{eq} value. For Ca(1), *U*_{ii} = 0.0076 Å² and *U*_{ij} = -0.0022 Å²; for Ca(2), *U*_{ii} = 0.0368 Å² and *U*_{ij} = 0.0091 Å² (*i* \neq *j*). ^e Hydrogen atom positions were calculated by the suite of computer programs SHELX-97⁴³ using C-H = 0.97 Å.

reflections for which $14^\circ < 2\theta < 22^\circ$, is $a = 24.966(4)$ Å. All unique reflections are 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(1) °C. An absorption correction was made empirically using a ψ scan. These corrections had little effect on the final R indices. Other details are the same as those previously reported.^{35,42}

Structure Determination. Full-matrix least-squares refinement⁴³ was done on *F*² using all data. It was initiated with the atomic parameters of the framework atoms (Si, Al, O(1), O(2), O(3), and O(4)) in dehydrated Ca₄₆-X·30C₃H₆.¹² These positions when refined anisotropically yielded *R*₁ = 0.20 and *wR*₂ = 0.70. *R*₁ = $(\sum(|F_o| - |F_c|)|)/\sum F_o$ and is calculated using 253 reflections with $F_o > 4\sigma(F_o)$; *wR*₂ = $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ is based on *F*² and is calculated using all 1153 unique reflections measured.

A Fourier difference electron-density function yielded two strong peaks at (0.0, 0.0, 0.0) and (0.2253, 0.2253, 0.2253), which are positions near framework oxygens normally occupied by cations. Isotropic refinement of the framework atoms with Ca²⁺ ions at these two positions converged to *R*₁ = 0.060 and *wR*₂ = 0.165. The occupancies at these two positions refined to 16.2(2) at Ca(1) and 28.7(3) at Ca(2).

An ensuing Fourier function revealed three more peaks at general positions of (0.344, 0.255, 0.269), (0.305, 0.257, 0.325), and (0.328, 0.208, 0.369). With occupancies constrained to be equal, refinement converged to 25.0(13) carbon atoms each at C(1), C(2), and C(3).

The thermal ellipsoids of Ca(2) became elongated in subsequent refinements, indicating the presence of two nonequivalent Ca²⁺ 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).

The occupancy numbers at Ca(1), Ca(2), 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), C(2), and C(3) were refining in the ratio of 1:3:3:3. The goodness of fit, $[\sum w(F_o^2 - F_c^2)^2/(m - s)]^{1/2}$, is 0.77; the number of observations, *m*, is 1153 (of these, 253 had $F_o > 4\sigma(F_o)$), and the number of parameters, *s*, is 82.

TABLE 2: Selected Interatomic Distances (Å) and Angles (deg)^a

	Å		deg
Si—O(1)	1.641(10)	O(1)—Si—O(2)	111.4(6)
Si—O(2)	1.688(11)	O(1)—Si—O(3)	108.5(5)
Si—O(3)	1.693(10)	O(1)—Si—O(4)	114.7(5)
Si—O(4)	1.644(10)	O(2)—Si—O(3)	106.7(5)
mean Si—O	1.667	O(2)—Si—O(4)	101.9(5)
Al—O(1)	1.673(11)	O(3)—Si—O(4)	113.3(5)
Al—O(2)	1.709(11)	O(1)—Al—O(2)	112.8(6)
Al—O(3)	1.693(10)	O(1)—Al—O(3)	108.1(5)
Al—O(4)	1.653(11)	O(1)—Al—O(4)	114.7(5)
mean Al—O	1.682	O(2)—Al—O(3)	107.1(5)
Ca(1)—O(3)	2.417(9)	O(2)—Al—O(4)	99.4(5)
Ca(2)—O(2)	2.272(9)	O(3)—Al—O(4)	114.5(5)
Ca(3)—O(2)	2.332(13)	Si—O(1)—Al	124.8(6)
		Si—O(2)—Al	140.6(6)
Ca(3)—C(1)	2.98(9)	Si—O(3)—Al	129.6(6)
Ca(3)—center	2.70	Si—O(4)—Al	167.6(7)
C(1)—C(2) ^b	1.55(5)	O(3)—Ca(1)—O(3)	87.0(3)/93.0(3)
C(2)—C(1) ^{cb}	1.54(5)	O(2)—Ca(2)—O(2)	118.7(4)
C(2)—C(3) ^b	1.65(4)	O(2)—Ca(3)—O(2)	114.0(5)
H(3b)····O(1)	2.52	C(1)—C(2)—C(1)'	129(3)
H(1) ^c ····O(4)	2.70	C(2)—C(1)—C(2)'	99(3)
		C(1)—C(2)—C(3)	141(3)
		C(3)—C(2)—C(1)'	85(3)

^a Numbers in parentheses are estimated standard deviations in the units of the least significant digit given for the corresponding value.

^b For comparison, the C—C ring and C—CH₃ distances are 1.397(1) and 1.505(5) Å, respectively, in C₉H₁₂(g).⁴⁶ ^c Hydrogen atom positions were calculated.⁴³

The final error indices converged to $R_1 = 0.046$ and $wR_2 = 0.128$. Atomic scattering factors⁴⁴ for Si, Al, O[−], C, and Ca²⁺ were used. All scattering factors were modified to account for anomalous dispersion.⁴⁵ The final structural parameters and selected interatomic distances⁴⁶ and angles are presented in Tables 1 and 2, respectively.

Discussion

Zeolite X is an aluminum-rich synthetic analogue of the naturally occurring mineral faujasite (FAU). The 14-hedron with 24 vertexes known as the sodalite cavity or β cage may be viewed as the principal building block of the aluminosilicate framework of the zeolite. These β cages are connected tetrahedrally at 6-rings by bridging oxygens (see Figure 1) to give double 6-rings (D6Rs, 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 vertexes 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 (β) cavity on the opposite side of one of the D6R's 6-rings from site I, II' inside the sodalite cavity near a single 6-ring (S6R, shared by a β 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 2-fold axis).^{47,48}

The average Si—O and Al—O bond distances in zeolite X are not sensitive to ion exchange and dehydration. The individual bond lengths, however, show marked variations: Si—O from 1.641(10) to 1.693(10) Å and Al—O from 1.653(11) to 1.709(11) Å (see Table 2). The individual Si—O and Al—O distances

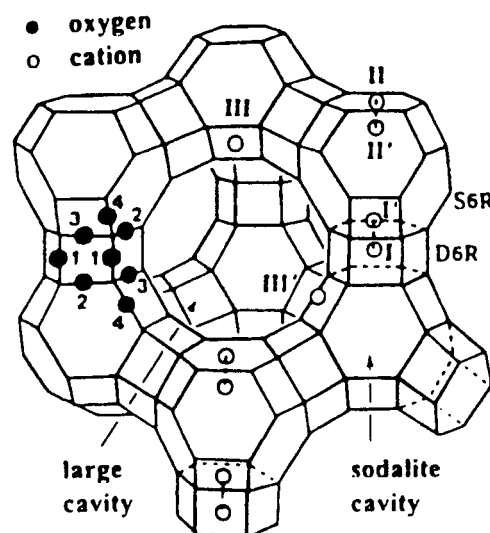


Figure 1. Stylized drawing of the framework structure of zeolite X. Near the center of each line segment is an oxygen atom. The different oxygen atoms are indicated by the numbers 1–4. Silicon and aluminum atoms alternate at the tetrahedral intersections, except that Si substitutes for about four of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

depend on Ca²⁺ coordination to framework oxygen. O(1) and O(4) are not involved in coordination; the Ca²⁺ ions at sites I and II coordinate only to O(2) and O(3). Accordingly, the Si—O(2), Al—O(2), Si—O(3), and Al—O(3) distances are lengthened (see Table 2). This effect is commonly seen in fully divalent cation-exchanged zeolite X.⁴⁹

In this structure, the mean Si—O and Al—O distances are relatively close to each other, 1.664 and 1.682 Å, respectively, which is indicative of a negligible to minor loss of Al from the zeolite framework during ion exchange.⁴⁰ The low pH of Ca²⁺ exchange appears to have introduced substantial antidomain structure into the zeolite single crystal.⁴⁰

In Ca₄₆—X·8C₉H₁₂, all Ca²⁺ ions are found at three different crystallographic sites of high occupancy. Sixteen Ca²⁺ ions at Ca(1) fill site I at the center of the D6Rs (see Figure 2). The octahedral Ca(1)—O(3) distance, 2.417(9) Å, is a little longer than the sum of the corresponding ionic radii, 0.99 + 1.32 = 2.31 Å,⁵⁰ indicating a reasonably good fit. In empty Ca₄₆—X, the Ca(1)—O(3) distance is similar, 2.429(8) Å.⁴⁹ The 22 cations at Ca(2) and the 8 at Ca(3) are located at two sites II in the supercage (Figures 3 and 4); each Ca²⁺ ion coordinates at 2.272(9) and 2.332(13) Å, respectively, to three O(2) framework oxygens.

The O(2)—Ca(2)—O(2) angle is 118.7(4)°, and the O(2)—Ca(3)—O(2) angle is 114.0(5)° (see Table 2). Because different O(2) coordinates have not been determined for these two situations, only an average O(2) position was used. The distance and angle involving Ca(3) are likely to be more in error than those involving Ca(2).

To coordinate to a mesitylene molecule, each Ca²⁺ ion at Ca(3) has moved 0.28 Å further into the supercage, further from their triads of three O(2) oxygens as compared with the corresponding Ca²⁺ position in dehydrated Ca₄₆—X⁴⁹ (see Figures 3 and 4). In this (small) way, these Ca²⁺ ions are able to coordinate more octahedrally to mesitylene (considering mesitylene to be tridentate). Similarly, in the crystal structures of the ethylene,⁷ acetylene,⁷ cyclopropane,¹² and benzene¹³ sorption complexes of dehydrated fully Ca²⁺-exchanged zeolite X, the Ca²⁺ ions at site II moved 0.11, 0.12, 0.16, and 0.25 Å further into the supercage, respectively, as compared with the

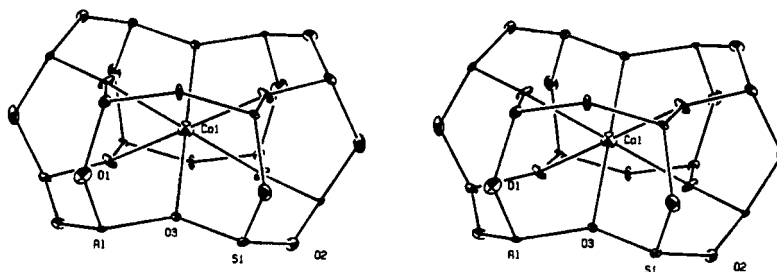


Figure 2. Stereoview of a double 6-ring. The ion at Ca(1) is shown at site I. Ellipsoids of 20% probability are used.

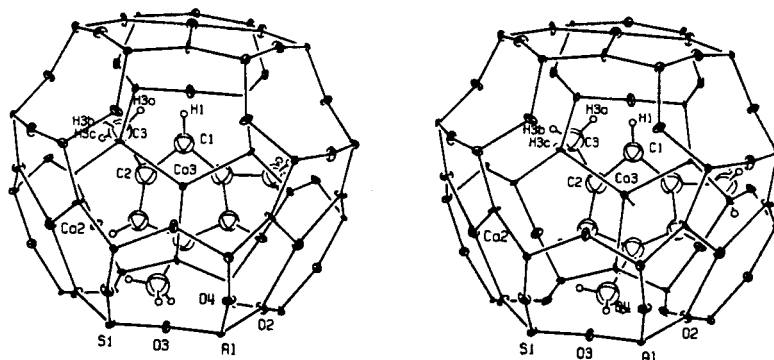


Figure 3. Stereoview of a sodalite cavity. Three Ca^{2+} ions are shown at Ca(2), and one Ca^{2+} ion is shown at Ca(3). The Ca^{2+} ion at Ca(3) coordinates to mesitylene. The Ca^{2+} ions at Ca(2) do not coordinate to mesitylene. Ellipsoids of 20% probability are used.

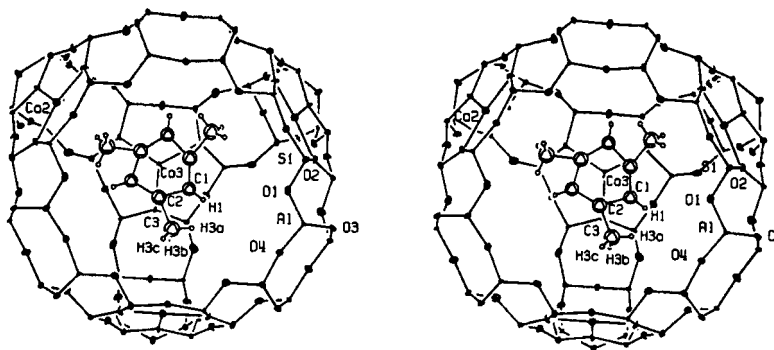


Figure 4. Stereoview of a supercage. Three Ca^{2+} ions at Ca(2) are shown. One Ca^{2+} ion at site II (at Ca(3)) coordinates to a mesitylene molecule. Ellipsoids of 20% probability are used.

corresponding position in dehydrated $\text{Ca}_{46}\text{-X}$. Compared with the previous structures,^{7,12,13} the deviation of the Ca^{2+} ions at site II from the 6-ring plane at O(2) into the supercage is larger than those in $\text{Ca}_{46}\text{-X}\cdot 30\text{C}_2\text{H}_2\text{S}$, $\text{Ca}_{46}\text{-X}\cdot 30\text{C}_2\text{H}_4$,⁷ $\text{Ca}_{46}\text{-X}\cdot 30\text{C}_3\text{H}_6$,¹² and $\text{Ca}_{46}\text{-X}\cdot 28\text{C}_6\text{H}_6$.¹³ It is reasonable that the interaction of Ca^{2+} with mesitylene is stronger than that with benzene because methyl groups are more electron-donating to the ring than hydrogen atoms are. As in $\text{Ca}_{46}\text{-X}\cdot 30\text{C}_2\text{H}_2\text{S}$ and $\text{Ca}_{46}\text{-X}\cdot 28\text{C}_6\text{H}_6$, the 16 site I Ca^{2+} ions also do not participate in sorption.

As a consequence of the movement of the Ca(3) ions more deeply into the supercage upon complexation, the Ca(3)–O(2) bonds have increased from 2.276(5) Å in dehydrated $\text{Ca}_{46}\text{-X}$ ⁴⁹ to 2.332(13) Å. The O(2)–Ca(2)–O(2) angle has correspondingly decreased from nearly trigonal planar at 118.3(2)° in dehydrated $\text{Ca}_{46}\text{-X}$ to 114.0(5)° in the mesitylene complex (see Table 2 and Figures 3 and 4). The 22 Ca^{2+} ions at Ca(2) that do not coordinate to mesitylene are recessed only 0.26(1) Å into the supercage from their O(2) plane; compared to dehydrated $\text{Ca}_{46}\text{-X}$,⁴⁹ each of these Ca^{2+} ions deviates 0.04 Å less from the plane of its three O(2) oxygens, to which it coordinates more trigonally.

Each supercage has accepted only one mesitylene molecule. Eight mesitylene molecules lie on 3-fold axes in the eight large cavities per unit cell, where each interacts facially with a Ca^{2+} ion (Ca^{2+} –mesitylene center = 2.70 Å). In contrast, two or three benzene molecules per supercage of $\text{Ca}_{46}\text{-X}\cdot 28\text{C}_6\text{H}_6$ ¹³ coordinate to Ca^{2+} . Twenty-two benzenes lie on 3-fold axes in the eight large cavities, where each interacts facially with a Ca^{2+} ion at site II (Ca^{2+} –benzene center = 2.76 Å). (Eight additional site II Ca^{2+} ions do not associate with the benzene molecules.¹³) It appears that the methyl groups of the mesitylene molecules prevent additional molecules from being sorbed into the supercage (see Figure 4): the sorption of a second mesitylene molecule per supercage at an equivalent site would give an unacceptably short methyl–methyl contact.

Six benzene molecules were found in the 12-ring planes (occupancy = 6 molecules/16 sites) of $\text{Ca}_{46}\text{-X}\cdot 28\text{C}_6\text{H}_6$; each hydrogen of these six benzenes is ~3.0 Å from three 12-ring oxygens.¹³ Mesitylene molecules are clearly too large to fit into 12-ring planes.

The Ca(2)–C bond distance is relatively long (Ca^{2+} –C = 2.98(9) Å), and the changes to the framework upon sorption are relatively small. The cell constant decreased slightly from

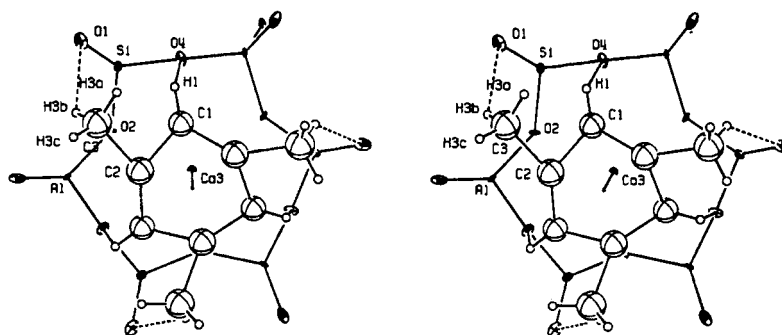


Figure 5. $\text{Ca}(\text{C}_9\text{H}_{12})_2^{2+}$ complex on the inner surface of a supercage is shown. Eight Ca^{2+} ions at Ca(3) coordinate to mesitylene molecules as shown. Three methyl hydrogen atoms, H(3b), interact weakly with O(1) oxygens at a distance of 2.52 Å, and three phenyl hydrogen atoms, H(1), interact weakly with O(4) at a distance of 2.70 Å. Altogether, each mesitylene molecule has six $\text{H}\cdots\text{O}$ interactions. Ellipsoids of 20% probability are used.

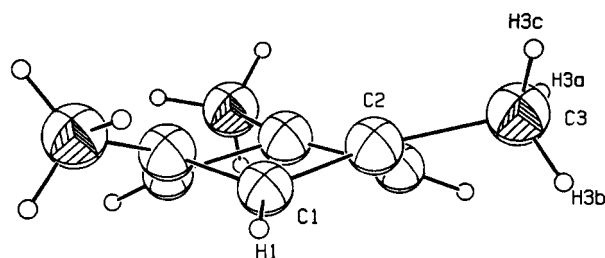


Figure 6. Side view of a sorbed (distorted) mesitylene molecule. Note that the plane of the methyl groups is above the C(2) plane, which is above the C(1) plane.

25.024(4) Å in dehydrated $\text{Ca}_{46}\text{-X}^{49}$ to 24.966(4) Å in its mesitylene complex.

Generally, the structural changes that occur in zeolites upon the sorption of guest molecules are small.⁶ In $\text{M}^{2+}_{46}\text{-X}$,^{7,12,49} for example, the cell constants decrease less than 0.3% upon sorption. Because the $\text{M}^{2+}\text{-C}$ approach distances are long, these interactions are weak. The mean Si-O and Al-O distances change very little. In most cases, the cation site distribution remained the same after sorption.

The closest approach of mesitylene to the zeolite framework involves $\text{H}(3\text{b})\cdots\text{O}(1)$ at a distance of 2.52 Å and $\text{H}(1)\cdots\text{O}(4)$ at a distance of 2.70 Å. (The hydrogen atom positions were not determined crystallographically but were calculated from the carbon positions.) These distances suggest significant electrostatic and van der Waals interactions; the sum of the van der Waals radii of oxygen and hydrogen is $1.4 + 1.2 = 2.6$ Å.⁵² These $\text{H}\cdots\text{O}$ guest-to-framework contacts are found in many organic sorption complexes of zeolites.⁶ Figures 4 and 5 suggest that the methyl groups are relatively locked into position and are not free to rotate.

Although the primary interaction is between the Ca^{2+} ion and the permanent electrical quadrupole moment of the hydrocarbon, the polarizable π -electron density of the hydrocarbon and the multiple interactions between the framework oxygens and the hydrocarbon hydrogens also contribute to the sorption of the unsaturated hydrocarbon in these complexes. In conjunction with the curved inner surface of the supercage, these interactions appear to have distorted the mesitylene molecules enough for these distortions to be crystallographically observable (see Figures 4–6 and Table 3), although crystallographic inaccuracies are evident. Contributing to the distortion is the decrease in the methyl hydrogen to ring hydrogen repulsive interactions. The bending of the mesitylene molecules suggests that the attraction between the rings and the Ca^{2+} ions has pulled the methyl groups closer to the framework than the distance of the energy minimum.

TABLE 3: Deviations of Atoms (Å) from (111) Planes

position	site	displacement
	at O(2) ^a	
Ca(2)	II	0.262
Ca(3)	II	0.584
C(1)		3.095
C(2)		3.467
C(3)		3.772
	at O(3) ^b	
Ca(1)	I	1.318

^a The positive displacements indicate that the ion or atom lies in the supercage. ^b The positive displacement indicates that the ion lies within a double 6-ring.

The sorbed mesitylene molecules appear to be distorted in the same way and to a similar extent as is half a molecule of [2.2.2](1,3,5)-cyclophane-1,9,17-triene.⁵¹ The 1,3,5 methyl groups are all on the same side of the benzene plane, and the three ring-carbon atoms to which they are bound are displaced by a smaller amount in the same direction (see Figure 6).

In summary, all Ca^{2+} ions are found at sites I and II: 16 per unit cell at site I and 30 per unit cell at site II. There are two kinds of site II Ca^{2+} ions: 8 coordinate to mesitylene molecules and 22 do not. Six hydrogen atoms of each of these mesitylene molecules are in van der Waals contact with framework oxygen atoms. Consistent with the observed color change upon sorption, the sorbed mesitylene molecules appear to be significantly deformed.

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Supporting Information Available: Crystallographic data for $\text{Ca}_{46}\text{Si}_{100}\text{Al}_{92}\text{O}_{384}\cdot 8\text{C}_9\text{H}_{12}$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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