

Crystal Structure of a Benzene Sorption Complex of Dehydrated Fully Cd²⁺-Exchanged Zeolite X

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The crystal structure of a benzene sorption complex of fully dehydrated Cd²⁺-exchanged zeolite X, Cd₄₆Si₁₀₀Al₉₂O₃₈₄·43C₆H₆ (*a*=24.880(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 Cd(NO₃)₂ for 3 d, followed by dehydration at 400 °C and 2 × 10⁻⁶ Torr for 2 d, followed by exposure to about 92 Torr of benzene vapor at 22 °C. The structure was determined in this atmosphere and refined to the final error indices *R*₁=0.054 and *R*_w=0.066 with 561 reflections for which *I* > 3σ(*I*). In this structure, Cd²⁺ ions are found at four crystallographic sites: eleven Cd²⁺ ions are at site I, at the centers of the double six-oxygen rings; six Cd²⁺ ions lie at site I', in the sodalite cavity opposite to the double six-oxygen rings; and the remaining 29 Cd²⁺ ions are found at two nonequivalent threefold axes of unit cell, sites II' (in the sodalite cavity) and site II (in the supercage) with occupancies of 2 and 27 ions, respectively. Each of these Cd²⁺ ions coordinates to three framework oxygens, either at 2.173(13) or 2.224(10) Å, respectively, and extends 0.37 Å into the sodalite unit or 0.60 Å 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-seven benzenes lie on threefold axes in the large cavities where they interact facially with the latter 27 site-II Cd²⁺ ions (Cd²⁺-benzene center=2.72 Å; occupancy=27 molecules/32 sites). The remaining sixteen benzene molecules are found in 12-ring planes; occupancy=16 molecules/16 sites. Each hydrogen of these sixteen benzenes is *ca.* 2.8/3.0 Å from three 12-ring oxygens where each is stabilized by multiple weak electrostatic and van der Waals interactions with framework 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.^{1,2} The system of benzene sorbed on synthetic faujasite-type zeolite has drawn significant attention in recent years. The location of benzene in sodium zeolite Y has been studied by powder neutron diffraction.^{3,4} At room temperature, the benzene molecules are "largely delocalized within the supercages" of zeolite Y, whereas at 4 K the benzene molecules are found at two distinct sites: one centered at the threefold axes of the unit cell near site II, and the other centered in the plane of the 12-ring window between adjacent supercages. Using high-speed X-ray powder diffraction methods, the influence of temperature on the sorption of benzene in K⁺, Ca²⁺ and Sr²⁺ exchanged Y-type zeolites was investigated.⁵ The ability of benzene to alter the cation distribution increases rapidly with the cation-benzene interaction energy. Using ²H NMR, Cheetham *et al.*⁶ found that C₆D₆ adsorbed in Ca-X (one molecule per supercage) is bound strongly at site II and interacts facially with Ca²⁺ so that rapid rotation about the sixfold axis of the sorbate is

observed in the temperature range 260-330 K. The nature of 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.⁷ 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.

This work was done to locate the sorbed C₆H₆ molecules by single-crystal diffraction methods at ambient temperature, to determine the cation shifts upon sorption, and to observe cation-sorbate interactions in a transition-metal exchanged zeolite. Crystal structure of a benzene sorption complex of dehydrated Cd²⁺-exchanged zeolite X is particularly interesting to study for three reasons: (1) Cd²⁺ is a powerful scatterer of X-rays, so these ions are relatively easy to locate, (2) ion exchange of Cd²⁺ ions into the zeolite is facile and complete, and (3) Cd²⁺ ions are expected to interact strongly with benzene molecules.

Experimental Section

Crystal Preparation. Large single crystals of zeolite Na-X, stoichiometry Na₄₀Si₁₀₀Al₉₂O₃₈₄, were prepared in St. Petersburg, Russia.⁸ One of these, a colorless octahedron about 0.20 mm in cross-section, was lodged in a fine Pyrex capillary. Aqueous 0.05 M Cd(NO₃)₂ was allowed to flow past the crystal at a velocity of 1.0 cm/s for 3 d. 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 benzene complex, the crystal was treated with *ca.* 92 Torr of zeolitically dried benzene for 3 d at 22(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 $a=24.880(6)$ 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. Of the 1386 unique reflections examined, only the 561 reflections for which $l > 3\alpha(l)$ were used in subsequent structure determination and refinement. 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 previously reported.^{9,10}

Structure Determination

Full-matrix least-squares refinement was initiated with the atomic parameters of the framework atoms [Si, Al, O(1), O(2), O(3) and O(4)] in dehydrated Cd₄₆-X.¹⁰ Isotropic refinement of the framework atoms converged to an unweighted R_1 index, $(\sum(F_o - |F_c|)/\sum F_o)$, of 0.52 and a weighted R_w index, $(\sum w(F_o - |F_c|)^2/\sum wF_o^2)^{1/2}$, of 0.58.

A difference Fourier function showed the positions of the Cd²⁺ ions at Cd(1), (0.0, 0.0, 0.0) with peak height $19.6 \text{ e}\text{\AA}^{-3}$,

at Cd(2), (0.233, 0.233, 0.233) with peak height $16.3 \text{ e}\text{\AA}^{-3}$, and at Cd(3), (0.068, 0.068, 0.068) with peak height $6.05 \text{ e}\text{\AA}^{-3}$. Isotropic refinement of the framework atoms, Cd(1), Cd(2) and Cd(3) converged to $R_1=0.141$ and $R_w=0.180$.

A subsequent difference Fourier synthesis indicated with a peak of height $1.77 \text{ e}\text{\AA}^{-3}$ that carbon atoms are at the general position (0.257, 0.322, 0.295). Least-squares refinement including this peak at C(1) with an isotropic temperature factor converged to $R_1=0.093$ and $R_w=0.109$. A subsequent difference Fourier synthesis indicated with a peak of height $1.38 \text{ e}\text{\AA}^{-3}$ that the remaining carbon atoms of these benzene molecules are at the general position (0.264, 0.287, 0.330). Least-squares refinement including this peak, C(2), isotropically, converged to $R_1=0.075$ and $R_w=0.080$. A later difference Fourier synthesis indicated with a peak of height $1.0 \text{ e}\text{\AA}^{-3}$ that carbon atoms of a second kind of benzene molecule are at the general position (0.477, 0.476, 0.550), C(3). Least-squares refinement including this peak isotropically, converged to $R_1=0.066$ and $R_w=0.071$. The thermal ellipsoid of Cd(2) became elongated in subsequent refinements, indicating the presence of two nonequivalent Cd²⁺ ions at this position. This position was split into Cd(2) at (0.207, 0.207, 0.207) and Cd(3) at (0.23, 0.23, 0.23). Anisotropic refinement of all atoms, except the carbon atoms which were refined isotropically, converged to $R_1=0.050$ and $R_w=0.058$.

The occupancy numbers at Cd(1), Cd(2), Cd(3), Cd(4), 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 Cd(2), 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 $R_1=0.054$ and $R_w=0.066$. The goodness-of-fit, $(\sum w(F_o - |F_c|)^2/(m-s))^{1/2}$, is 1.78, where m (561) is the number of observations and s (77) is the number of

Table 1. Positional, thermal^a, 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)		-527(1)	1234(2)	353(1)	204(21)	122(19)	124(21)	-1(20)	-11(19)	-31(21)		96.0
Al	96(g)		-534(2)	368(2)	1223(2)	151(21)	97(21)	96(21)	-2(20)	5(21)	-29(22)		96.0
O(1)	96(g)		-1077(4)	7(5)	1049(4)	306(66)	300(66)	260(62)	85(56)	-3(48)	-45(55)		96.0
O(2)	96(g)		-20(4)	-18(5)	1466(4)	182(53)	282(57)	238(55)	63(50)	-2(49)	-43(38)		96.0
O(3)	96(g)		-293(4)	656(4)	637(5)	409(71)	271(65)	304(64)	108(62)	134(63)	80(56)		96.0
O(4)	96(g)		-664(4)	800(4)	1711(4)	379(66)	180(56)	182(56)	46(58)	-19(58)	-9(49)		96.0
Cd(1)	16(c) I		0	0	0	81(6)	81(6)	81(6)	6(9)	6(9)	6(9)	11.5(2)	11.0
Cd(2)	32(e) II(a)		2308(1)	2308(1)	2308(1)	294(6)	294(6)	294(6)	144(8)	144(8)	144(8)	27.3(3)	27.0
Cd(3)	32(e) I'		710(3)	710(3)	710(32)	173(25)	173(25)	173(25)	72(30)	72(30)	72(30)	6.5(3)	6.0
Cd(4)	32(e) II(b)		2078(7)	2078(7)	2078(7)	126(710)						2.5(3)	2.0
C(1)	96(g)		2593(19)	3241(18)	2925(11)	1906(224)						81.9(9)	81.0
C(2)	96(g)		2618(20)	2899(22)	3368(18)	2003(236)						81.9(9)	81.0
C(3)	96(g)		4776(24)	4765(23)	5502(14)	1978(208)						97.0(9)	96.0
H(1) ^e	96(g)		2200	2865	3421								81.0
H(2) ^e	96(g)		3743	2396	2922								81.0
H(3) ^e	96(g)		4175	5202	5527								96.0

^a 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. ^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 $U_{iso} = B_{iso}/8\pi^2$. ^e These hydrogen coordinates were calculated using the best-plane coordinates for benzene(1). ^f Calculated hydrogen coordinates for benzene(2).

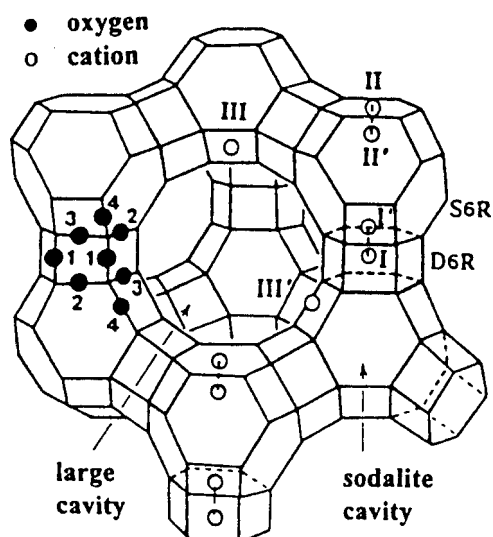


Figure 1. Stylized drawing of the framework structure of zeolite X. Near the center of each line segment is an oxygen atom. The different oxygen atoms are indicated by the numbers 1 to 4. Silicon and aluminum atoms alternate at the tetrahedral intersections, except that Si substitutes for about four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

variables in least-squares refinement. The final difference Fourier function was featureless.

Atomic scattering factors¹¹ for Si, Al, O⁻, C, and Cd²⁺ were used. All scattering factors were modified to account for anomalous dispersion.¹² The final structural parameters and 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 β cage may be viewed as the principal building block of the aluminosilicate framework of the zeolite. These β cages are connected tetrahedrally at six-rings by bridging oxygens (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 half-way between each pair of Si and Al atoms but are displaced from those points to give near tetrahedral angles about Si and Al.

Exchangeable cations, which balance the negative charge of the aluminosilicate framework, are found within the zeolite's cavities. They are usually found at the following sites shown in Figure 1: site I at the center of a D6R, I' in the sodalite (β) cavity on the opposite side of one of the D6R's six-rings from site I, II' inside the sodalite cavity near a single six-ring (S6R, 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 twofold axis).^{13,14}

The averaged bond distances of the Si-O (1.656 Å) and

Table 2. Selected interatomic distances (Å) and angles(deg)^a for framework atoms and calcium ions

Si-O(1)	1.622(12)	O(1)-Si-O(2)	112.4(4)
Si-O(2)	1.674(12)	O(1)-Si-O(3)	107.5(6)
Si-O(3)	1.700(12) ^a	O(1)-Si-O(4)	111.8(6)
Si-O(4)	1.628(11)	O(2)-Si-O(3)	105.3(6)
Mean	1.656	O(2)-Si-O(4)	106.2(6)
		O(3)-Si-O(4)	113.3(6)
Al-O(1)	1.675(12)		
Al-O(2)	1.710(12) ^b	O(1)-Al-O(2)	113.2(6)
Al-O(3)	1.732(12) ^b	O(1)-Al-O(3)	106.4(6)
Al-O(4)	1.653(12)	O(1)-Al-O(4)	112.5(6)
Mean	1.693	O(2)-Al-O(3)	105.6(6)
		O(2)-Al-O(4)	104.6(6)
Cd(1)-O(3)	2.390(11)	O(3)-Al-O(4)	114.5(6)
Cd(2)-O(2)	2.224(10)		
Cd(3)-O(3)		O(2)-Cd(1)-O(3)	92.5(4)/87.5(4)
Cd(4)-O(2)	2.504(11)	O(2)-Cd(2)-O(2)	112.9(4)
Si-O(1)-Al	134.0(7)	O(2)-Cd(3)-O(2)	82.7(4)
		O(2)-Cd(4)-O(2)	117.1(4)
		Si-O(2)-Al	135.8(7)
		Si-O(3)-Al	125.5(7)
		Si-O(4)-Al	156.0(8)

^aNumbers in parentheses are estimated standard deviations in the units of the least significant digit given for the corresponding value. ^bThese distances are longer than the others in this group because O(2) and O(3) bind to Cd²⁺. O(1) and O(4) are two-coordinate; O(2) and O(3) are three-coordinate.

Al-O (1.693 Å) are not sensitive to ion exchange and dehydration. The individual bond lengths, however, show marked variations: Si-O from 1.622(12) to 1.700(12) Å and Al-O from 1.653(12) to 1.732(12) Å (see Table 2). The individual Si-O and Al-O distances depend on Cd²⁺ coordination to framework oxygen. O(1) and O(4) are not involved in coordination; Cd²⁺ 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.¹⁵

In Cd₄₆-X·43C₆H₆, all Cd²⁺ ions are found at four different crystallographic sites of high occupancy. The 11 Cd²⁺ ions at Cd(1) occupy site I at the center of the D6R's (see Figure 2). The octahedral Cd(1)-O(3) distance, 2.390(11) Å, is a little longer than the sum of the corresponding ionic radii, 0.97+

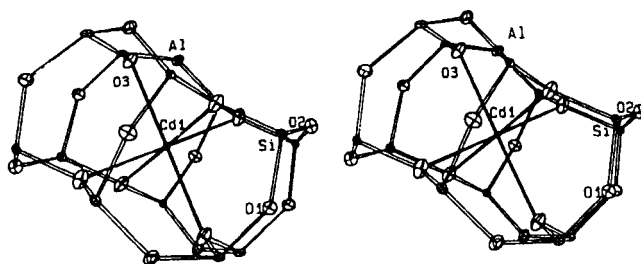


Figure 2. Stereoview of a double six-ring. The ion at Cd(1) is shown at site I. Ellipsoids of 20% probability are used.

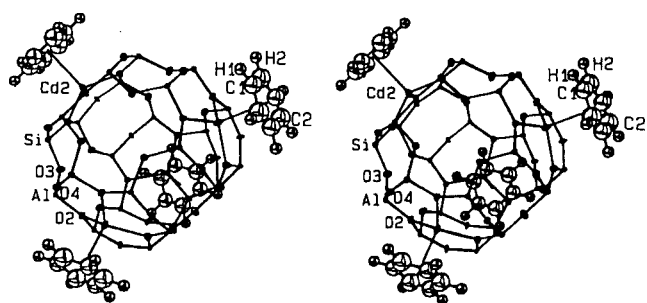


Figure 3. Stereoview of a sodalite cavity. Four Cd²⁺ ions are shown at Cd(2). Each coordinates to a benzene molecule. Ellipsoids of 20% probability are used.

Table 3. Selected interatomic distances (Å) and angles (deg)^a involving sorbed benzene molecules

Benzene(1)		Benzene(1)-Framework	
C(1)-C(2)	1.39(8)	C(1)-O(1)	3.98(5)
C(2)-C(1)	1.13(8)	C(1)-O(2)	3.48(5)
C(1)-H(1)	1.085	C(1)-O(4)	3.76(5)
C(2)-H(2)	1.085	C(2)-O(1)	3.98(5)
		C(2)-O(2)	3.54(45)
		C(2)-O(4)	3.77(6)
Benzene(2)		Benzene(2)-Framework	
C(3)-C(3)	1.49(6)	H(1)-O(1)	3.47
C(3)-H(3)	1.085	H(1)-O(2)	3.02
		H(1)-O(4)	3.21
Benzene(1)-Cd(2)		Benzene(1)-Cd(2)	
C(1)-Cd(2)	2.87(5)	H(2)-O(1)	3.47
C(2)-Cd(2)	3.11(5)	H(2)-O(2)	3.02
Center-Cd(2)	2.72	H(2)-O(4)	3.21
C(1)-C(2)-C(1)'	132(5)	C(3)-O(1)	3.84(6)/3.86(6)
C(2)-C(1)-C(2)'	103(5)	C(3)-O(4)	3.87
C(3)-C(3)'-C(3)''	119(3)	H(3)-O(1)	2.81
		H(3)-O(4)	2.96/2.99

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

1.32=2.29 Å,¹⁶ indicating a reasonably good fit. The 27 at Cd(2) are located at site II in the supercage and the 2 at Cd(4) are located at site II' in sodalite cavity; each coordinates at 2.224(10) Å and 2.173(13) Å, respectively, to three O(2) framework oxygens. The O(2)-Cd(2)-O(2) angle is 112.9(4)^o and the O(2)-Cd(4)-O(2) angle is 117.1(4)^o (see Table 2).

Crystallographically there are two kinds of benzene molecules. The first, benzene(1), is on a threefold axis deep inside the supercage with 162 carbon atoms (27 molecules of C₆H₆) per unit cell at two sites, C(1) and C(2); these interact facially with the 27 Cd²⁺ ions at site II (Cd(3)-benzene center=2.72 Å) (Figure 3). Benzene(1) deviates insignificantly from planarity (see Table 4). The benzene(1) has relatively high thermal motion, its geometry is unrealistically puckered (see Table 3); this puckering is not crystallographically significant. (C(1)-C(2)=1.13(8) and C(2)-C(1)=1.39(8) Å; C(1)-C(2)-C(1)=103(5)^o and C(2)-C(1)-C(2)=132(5)^o) (see Table 3 and Figures 3, 4 and 5). The C-C distance in C₆H₆(g) is 1.397(1) Å.¹⁷ The positions of the hydrogen atoms, H(1) and H(2), were calculated by the computer system MolEN¹⁸ using C-H=1.085 Å.

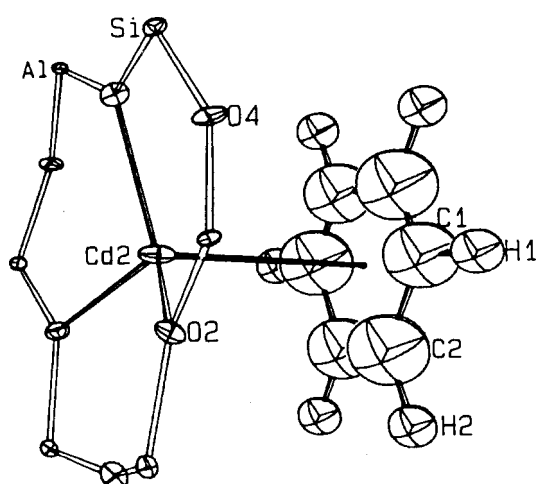


Figure 4. A Cd(C₆H₆)₂²⁺ complex on the inner surface of a supercage is shown. Ellipsoids of 20% probability are used. Twenty-seven Cd²⁺ ions at Cd(2) coordinate to benzene molecules as shown.

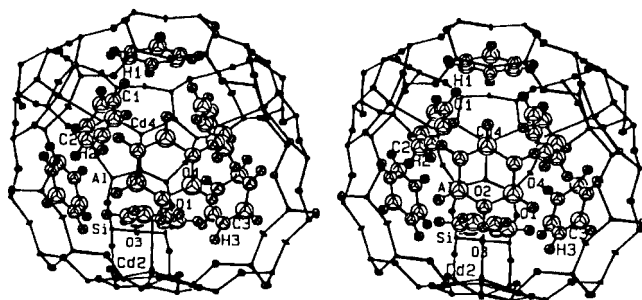


Figure 5. Stereoview of a supercage. Three Cd²⁺ ions at Cd(2) are shown. Each coordinates to a benzene(1) molecule. The Cd²⁺ ion at Cd(4) does not coordinate to benzene. Four benzene(2) molecules are shown at 12-ring centers. Ellipsoids of 20% probability are used.

The coordination of benzene(1) has caused Cd(3) to move *ca.* 0.41 Å along its threefold axis more deeply into the supercage from three O(2) plane (see Figure 3 and Table 5), compared to its position in dehydrated Cd₄₆-X.¹⁰ In this small way, these Cd²⁺ ions are able to coordinate more octahedrally to benzene(1) (considering benzene to be tridentate). The deviation of these Cd²⁺ ions from the six-ring plane at O(2) into the supercage is larger than those in Cd₄₆-X·30C₂H₂,¹⁹ Cd₄₆-X·29.5C₂H₄,²⁰ and Cd₄₆-X·30CO.²¹

Table 4. Deviations of Atoms (Å) from (111) Planes

Position	Site	Displacement
at O(2) ^a		
Cd(2)	II(a)	0.60
Cd(4)	II(b)	-0.37
C(1)		3.24
C(2)		3.41
at O(3) ^b		
Cd(1)	I	1.44
Cd(3)	I'	-1.62

^a A positive displacement indicates that the ion lies in the supercage. ^b A positive displacement indicates that the ion lies at site I in a double six-ring.

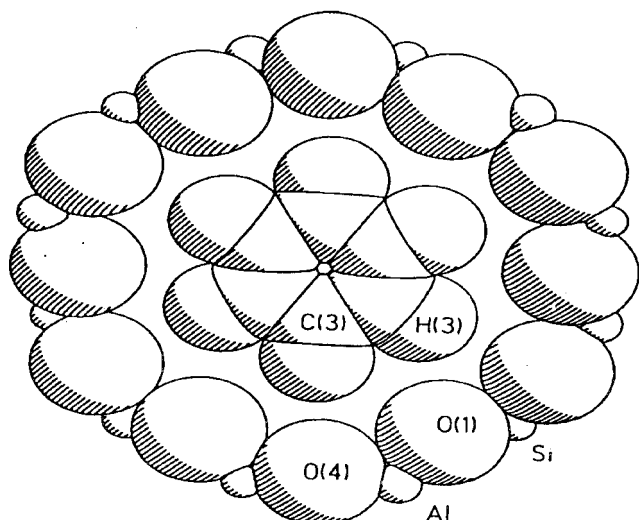


Figure 6. Van der Waals view of a 12-ring containing a benzene (2) molecule. Six of the 16 12-rings per unit cell are so occupied. The van der Waals radii used for oxygen and hydrogen are 1.40 and 1.20 Å, respectively. The positions plotted are those found crystallographically except for those of the hydrogen atoms: the H (3) coordinates were calculated from the 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 H...O interactions. The fit is remarkable. The view is along (111); the center is at (0.5, 0.5, 0.5); the symmetry is $\bar{3}$.

This and the Cd(2)-O(2) bond distances (see Table 2) suggest that, in binding to the benzene(1) molecule, the interaction between Cd(3) and the O(2) framework oxygens is slightly reduced. The benzene(1) site is less than fully occupied (27/32) and the same fraction of the Cd²⁺ ions at the sites II bind to benzene(1). The two Cd²⁺ ions at Cd(4) which do not coordinate to benzene(1) are recessed only 0.37(1) Å into the sodalite cavity from their O(2) plane.

The closest approach between benzene(1) and the zeolite framework involves the H(2) hydrogen atom and O(1) at a distance 3.02 Å, suggestive of a very weak electrostatic interaction.

The benzene(1) sorption site is similar to those observed in Na-Y⁴ at a loading level of 2.6 molecules per supercage, and in Ca-X⁶ with one molecule per supercage. Cheetham *et al.*,⁶ by studying Ca-X with sorbed C₆D₆ by ²H NMR, confirmed that deuterated benzene is bound strongly at site II, and that it interacts facially with calcium so that rapid rotation about the six-fold axis of the sorbate is observed in the temperature range 260-330 K. The activation energy for this rotation is 4.9 kJmol⁻¹. The precise nature of the cation-benzene interaction is unclear, but charge-quadrupolar terms are believed to be important.²² The stability of this site is believed to be due more to a quadrupolar than to a π -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 (C(3)-C(3) = 1.49(3) Å and C(3)-C(3)-C(3) = 119(3)^o). There are strong interactions between the hydrogens of benzene(2) and the oxygens of the 12-ring window (H(3)-O(1) = 2.81 Å and H(3)-

O(4) 2.96/2.99 Å). 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 close to the geometry of benzene molecule.¹⁷

Benzene usually occupies 12-rings only at high loadings.^{23,24} The observation of simultaneous occupation at the six- and in the 12-ring sites is in excellent agreement with previous neutron diffraction results.⁴ 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.

In summary, 46 Cd²⁺ ions occupy sites I, I', II, and II'; 11 per unit cell at sites I, 6 at site I', 2 at site II' and the remaining 27 at sites II. There are also two kinds of benzene molecules. The first kind (27 benzene molecules) coordinate facially to Cd²⁺ ions at site II in the supercage. The second kind (16 molecules) fill the 16 12-ring sites per unit cell. Each of these 16 benzene molecules is held in place by 18 van der Waals (each hydrogen approaches three framework oxygens) and weakly electrostatic interactions.

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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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Frequency-Distance Responses in SECM-EQCM: A Novel Method for Calibration of the Tip-Sample Distance[§]

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The frequency response on the tip-sample distance in scanning electrochemical microscopy (SECM) that is combined with an electrochemical quartz crystal microbalance (EQCM) is described. The oscillation frequency of the EQCM increases rapidly when the SECM tip is very close to the substrate electrode surface. This frequency increase is reproducible regardless of the current feedback in SECM, which is attributed to the stress caused by the tip pressing the quartz crystal. It is useful to calibrate the tip-sample distance with respect to the frequency change when a combined system of SECM and EQCM (SECM-EQCM) is used. This method could be applied to several cases such as rigid metal electrode and non-conducting or partially conducting polymer coating prepared on the quartz crystal regardless of the feedback current.

Introduction

The electrochemical quartz crystal microbalance technique¹ is a standard tool in obtaining electrochemical information at the electrode surface as well as mass transport information, which involves the movement of solvent molecules. It is based on the frequency change upon the mass change on the electrode surface. The relation between the mass change, and the corresponding frequency change is given by the Sauerbrey equation.²

In the case that there are stresses on the surface of quartz crystal, the frequency change increases with the stress. The total frequency shift Δf can be given by³

$$\Delta f / f_0 = K \Delta S / \tau_q - \Delta M / (\rho_q \tau_q), \quad (1)$$

where f_0 is the original shear resonant frequency in Hz, Δf is the frequency shift given by the new resonant frequency minus f_0 after the crystal resonator experiences the thin-film effects, and ΔM is the change in areal mass density (kg/m^2) of the film. ΔS is the change in the integral lateral stress in the thin film that is assumed isotropic and the parameter S is called the integrated stress given in N/m . ρ_q is the mass density of quartz ($2.65 \times 10^{-3} \text{ kg}/\text{m}^3$), τ_q is the thickness of

quartz plate in m, and K is $2.75 \times 10^{-11} \text{ m}^2/\text{N}$. Hence, a positive ΔS results in a frequency increase meaning an addition of tension to the film; however, a positive ΔM results in frequency decrease meaning an addition of mass to the thin film.

The scanning electrochemical microscopy⁴ is used frequently in examining the transport behavior of redox species at the electrode surface adopting techniques.^{5,6} An ultramicro-electrode (a tip electrode) employed in SECM measures the feedback current while it scans over the substrate electrode surface keeping the tip electrode close in few micrometers to the substrate or moves back and forth. The resultant tip current depending on the tip position can give images of electrode surface or information on electrochemical activity. Numerous papers⁵⁻²¹ have demonstrated its diverse potential. Recently, Bard *et al.*⁹ reported detection of a redox current from a single redox molecule via a positive feedback mode.

In SECM, it is very important to calibrate the tip-to-sample gap distance. For this purpose, a reversible redox couple is usually utilized in the solution between the tip and substrate, which are set at potentials reduction (or oxidation) and re-oxidation (or re-reduction) of the redox couple can take place, respectively. In the feedback mode of SECM, the tip-sample distance is usually determined by the observed current ratio, $I_T/I_{T,\text{inf}}$, based on theoretical curves,^{5,6} when the tip-sample distance is of the order of tip electrode radius. Here I_T is the tip current and $I_{T,\text{inf}}$ is the tip current when the tip is moved to a position far from the substrate. $I_T/I_{T,\text{inf}}$ is a

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