

Crystal Structure of an Ethylene Sorption Complex of Cd²⁺-Exchanged Zeolite X, Cd₄₆Si₁₀₀Al₉₂O₃₈₄·29.5C₂H₄

Young Hoon Yeom and Yang Kim*

Department of Chemistry, Pusan National University, Pusan 609-735, Korea

Seung Hwan Song

Department of Chemical Engineering, Deonseo University, Pusan 616-010, Korea

Karl Seff*

Department of Chemistry, University of Hawaii, 2545 The Mall, Honolulu, Hawaii 96822

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The crystal structure of an ethylene sorption complex of anhydrous fully Cd²⁺-exchanged zeolite X, Cd₄₆Si₁₀₀Al₉₂O₃₈₄·29.5C₂H₄ ($a = 24.864(6)$ Å), has been determined by single-crystal X-ray diffraction techniques in the cubic space group $Fd\bar{3}$ at 21(1) °C. A crystal of Cd₄₆-X was dehydrated at 450 °C and 2×10^{-6} Torr for 2 days followed by exposure to ca. 150 Torr of dry ethylene gas at 21(1) °C. The structure was determined in this atmosphere and refined to the final error indices $R_1 = 0.046$ and $R_w = 0.054$ with 740 reflections for which $I > 3\sigma(I)$. At site I (at the centers of the double six-rings), 15.5 octahedrally coordinated Cd²⁺ ions are found per unit cell (Cd–O = 2.350(6) Å). Only one Cd²⁺ ion (trigonal) is found at site I' (Cd–O = 2.503(6) Å). At site II (in the supercage), 29.5 Cd²⁺ ions are found (Cd–O = 2.221(6) Å). Each of these site-II Cd²⁺ ions is recessed 0.50(1) Å into the supercage from the plane of the three oxygens to which it is bound. To complete its distorted tetrahedral coordination, each coordinates laterally (symmetrically) to an ethylene molecule (counted as monodentate) in the supercage (Cd–C = 2.70(4) Å and C=C = 1.26(5) Å). No other ethylene molecules are sorbed.

Introduction

Exchangeable transition-metal ions in evacuated zeolites are generally coordinatively unsaturated. To relieve their coordinative unsaturation in zeolite A, the cations complex readily with a variety of guest molecules such as CO,¹ C₃H₆,² NO₂,³ H₂S,⁴ CS₂,⁵ NH₃,^{6,7} C₂H₄,^{8–10} and C₂H₂.^{11–13}

The crystal structure of dehydrated fully Cd²⁺-exchanged zeolite X, Cd₄₆Si₁₀₀Al₉₂O₃₈₄ (Cd₄₆-X), was determined by single-crystal X-ray diffraction techniques.¹⁴ There Cd²⁺ ions occupy only sites I and II. In the structures of Cd₄₆-X·28CO¹⁵ and Cd₄₆-X·28C₂H₂,¹⁶ Cd²⁺ ions are located at sites I, I', and II. To associate with a sorbed molecule and to achieve a more tetrahedral geometry, each of the 28 Cd²⁺ ions at site II has moved somewhat more deeply into the supercage in each structure.

The same work was done with Mn₄₆-X. In Mn₄₆-X·30CO¹⁷ and Mn₄₆-X·30C₂H₄,¹⁷ Mn²⁺ ions are located at only two crystallographic sites (I and II). Each of the 30 Mn²⁺ ions at site II associates with a CO or a C₂H₄ molecule, respectively, and has moved further into the supercage from the plane of its six-ring to do so.

Carter *et al.* studied the sorption of ethylene at room temperature onto variously ion-exchanged synthetic near-faujasites by infrared spectroscopy and by microcalorimetry.¹⁸ They found that C₂H₄ molecules complex laterally to give π complexes of symmetry C_{2v}. Of the transition-metal ions examined, Ag⁺ and Cd²⁺ were found to hold C₂H₄ most strongly; furthermore, the sorbed ethylene molecule is reported to be freely rotating in all the cases except in their complexes with Ag⁺ and Cd²⁺.

Hydrocarbon sorption structures of Cd²⁺-exchanged zeolite A have been studied. In dehydrated Cd₆-A, four ethylene¹⁰ or four acetylene¹³ molecules are sorbed per unit cell. Each of four Cd²⁺ ions lies on a 3-fold axis in the large cavity of the unit cell, close to three equivalent and trigonally arranged zeolite oxygen atoms and symmetrically close to both carbon atoms of the C₂H₄ or C₂H₂ molecules.

This work was done to locate the sorbed C₂H₄ molecules, to determine the cation shifts upon sorption, to observe cation–sorbate interactions, and perhaps to detect the resultant changes in the geometry of C₂H₄ upon sorption into Cd²⁺-exchanged zeolite X.

Experimental Section

Large single crystals of sodium zeolite X, stoichiometry Na₉₂-Si₁₀₀Al₉₂O₃₈₄, were prepared in St. Petersburg, Russia.¹⁹ One of these, a colorless octahedron about 0.25 mm in cross section, was lodged in a fine Pyrex capillary.

An exchange solution of Cd(NO₃)₂ and Cd(O₂CCH₃)₂ in the mole ratio of 1:1 with a total concentration of 0.05 M was allowed to flow past the crystal at a velocity of 1.0 cm/s for 5 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 450 °C at a constant pressure of 2×10^{-6} Torr. Finally, the system was maintained at this state for 48 h. After being cooled to room temperature, the crystal remained colorless. To prepare the ethylene complex, the crystal was treated with 150 Torr of zeolitically dried ethylene gas for 1 h at 21(1) °C. The resulting black crystal, still in its ethylene atmosphere, was sealed in its capillary by torch.

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

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TABLE 1: Positional, Thermal,^a and Occupancy Parameters for Cd₄₆-X·29.5C₂H₄

atom	Wyckoff			<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁ ^b (<i>U</i> _{iso})	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃	occupancy ^c	
	posn	site											varied	fixed
Si	96(g)			-526(1)	1229(1)	339(2)	143(12)	75(11)	104(12)	-8(11)	-9(11)	-11(11)		96.0
Al	96(g)			-547(1)	378(1)	1214(1)	120(13)	93(13)	71(12)	-1(11)	-13(12)	-23(12)		96.0
O(1)	96(g)			-1106(2)	19(3)	1046(3)	153(35)	206(35)	146(33)	-34(31)	24(27)	-26(31)		96.0
O(2)	96(g)			-23(3)	-25(3)	1459(2)	211(32)	172(31)	174(32)	62(32)	4(31)	-4(31)		96.0
O(3)	96(g)			-318(3)	655(3)	604(3)	156(34)	111(32)	154(33)	22(29)	53(30)	17(27)		96.0
O(4)	96(g)			-648(3)	830(3)	1712(3)	269(38)	105(33)	98(32)	-18(31)	28(31)	-56(27)		96.0
Cd(1)	16(c)	I		0	0	0	107(3)	107(3)	107(3)	7(4)	7(4)	7(4)	15.8(1)	15.5
Cd(2)	32(e)	I'		685(14)	685(14)	685(14)	371(100)	371(100)	371(100)	378(123)	378(123)	378(123)	1.4(1)	1.0
Cd(3)	32(e)	II		2285(1)	2285(1)	2285(1)	231(3)	231(3)	231(3)	80(4)	80(4)	80(4)	28.9(1)	29.5
C	96(g)			2969(20)	2667(15)	3058(17)	1521(127) ^d						64(2)	59.0

^a Positional and thermal parameters are given ×10⁴. 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[-2π²(h²(a*)²U₁₁ + k²(b*)²U₂₂ + l²(c*)²U₃₃ + 2hk(a*b*)U₁₂ + 2hl(a*c*)U₁₃ + 2kl(b*c*)U₂₃]. ^c Occupancy factors are given as the number of atoms or ions per unit cell. ^d U_{iso} = (B_{iso}/8π²).

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. The unit cell constant at 21-(1) °C, determined by least-squares refinement of 25 intense reflections for which 14° < 2θ < 22°, is *a* = 24.864(6) Å. All unique reflections for which 2θ < 50° were recorded. Of the 1368 reflections examined, only the 740 reflections for which *I* > 3σ(*I*) were used in subsequent structure determination. An absorption correction (μ = 1.96 mm⁻¹, ρ_{cal} = 1.126 g/cm³, and *F*(000) = 8648) was made empirically using a Ψ 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.⁴

Structure Determination

Full-matrix least-squares refinement was initiated by using the atomic parameters of the framework atoms [Si, Al, O(1), O(2), O(3), and O(4)] in dehydrated Cd₄₆-X.¹⁴ Anisotropic refinement of the framework atoms converged to an unweighted *R*₁ index, (Σ|*F*_o - |*F*_c||)/Σ*F*_o, of 0.51 and a weighted *R*_w index, (Σw(*F*_o - |*F*_c||)²/Σw*F*_o²)^{1/2}, of 0.57.

A difference Fourier function showed the positions of the Cd²⁺ ions at Cd(1), (0.0, 0.0, 0.0) with peak height 4.2 e Å⁻³, and at Cd(3), (0.226, 0.226, 0.226) with peak height 3.2 e Å⁻³. Anisotropic refinement of framework atoms and isotropic refinement of Cd(1) and Cd(3) converged to *R*₁ = 0.057 and *R*_w = 0.076.

A subsequent difference Fourier synthesis showed the position of the Cd²⁺ ion at Cd(2), (0.07, 0.07, 0.07) with peak height 0.7(2) e Å⁻³. Least-squares refinement as above including Cd(2) anisotropically converged to *R*₁ = 0.047 and *R*_w = 0.058. A later difference Fourier synthesis indicated with a peak of height 0.6 e Å⁻³ that the carbon atoms of the ethylene molecules are at the general position (0.300, 0.290, 0.289). Anisotropic refinement of all atoms, except that carbon atoms of the ethylene molecules which were refined isotropically, converged to *R*₁ = 0.045 and *R*_w = 0.053. The Hamilton significance test²⁰ shows that these carbon atoms are reliably determined at a level far greater than 99.5%.

The association of one C₂H₄ molecule with each Cd(3) ion was consistent with the refined occupancies (see Table 1). The movement of the Cd(3) position approximately 0.31 Å further into the supercage as compared to empty Cd₄₆-X¹⁴ (to a near-tetrahedral four-coordinate position) supports this result. Accordingly, the occupancy numbers at Cd(1), Cd(2), Cd(3), and C were fixed by the assumption of stoichiometry, the requirement of neutrality, and the avoidance of impossibly short

TABLE 2: Selected Interatomic Distances (Å) and Angles (deg)^a for Cd₄₆-X·29.5C₂H₄

Si-O(1)	1.599(7)	O(1)-Si-O(2)	111.9(4)
Si-O(2)	1.640(7) ^b	O(1)-Si-O(3)	108.0(3)
Si-O(3)	1.656(7) ^b	O(1)-Si-O(4)	111.5(4)
Si-O(4)	1.593(7)	O(2)-Si-O(3)	106.4(3)
mean	1.622	O(2)-Si-O(4)	106.8(4)
Al-O(1)	1.704(7)	O(3)-Si-O(4)	112.1(3)
Al-O(2)	1.750(7) ^b	O(1)-Al-O(2)	113.1(3)
Al-O(3)	1.761(7) ^b	O(1)-Al-O(3)	104.9(3)
Al-O(4)	1.691(7)	O(1)-Al-O(4)	113.9(3)
mean	1.726	O(2)-Al-O(3)	106.5(3)
Cd(1)-O(3)	2.350(6)	O(2)-Al-O(4)	103.6(3)
Cd(2)-O(3)	2.503(6)	O(3)-Al-O(4)	114.8(3)
Cd(3)-O(2)	2.221(6)	Si-O(1)-Al	130.2(4)
Cd(3)-C	2.70(4)	Si-O(2)-Al	136.1(4)
C=C	1.26(5)	Si-O(3)-Al	125.4(4)
		Si-O(4)-Al	160.3(5)
		O(3)-Cd(1)-O(3)	90.3(2), 89.7(2)
		O(3)-Cd(2)-O(3)	84.3(2)
		O(2)-Cd(3)-O(2)	115.1(3)

^a Numbers in parentheses are esd's in the units of the least significant digit given for the corresponding value. ^b These 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.

intercations contacts at the values shown for the nonframework positions in the fixed-occupancy column of Table 1. 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 = 0.046 and *R*_w = 0.054. The goodness-of-fit = (Σw(*F*_o - |*F*_c||)²/(*m* - *s*)^{1/2}) = 2.81, where *m* (740) is the number of observations and *s* (67) is the number of variables in least-squares refinement.

A subsequent difference Fourier function revealed six small peaks of heights from 0.52 to 0.21 e Å⁻³. The largest (0.201, 0.199, 0.199, height = 0.52(2) e Å⁻³) was 2.3 Å from O(2). In least-squares refinement with *B*_{iso} fixed, neither it nor the nearest 3-fold-axis position was stable. The second peak (0.249, 0.496, 0.248, height = 0.26(2) e Å⁻³) was far from any other atom, and the third (0.125, 0.125, 0.075, height = 0.24(2) e Å⁻³) at 2.0 Å from Cd(2) was also unstable in least squares.

Atomic scattering factors²¹ for Si, Al, O⁻, C, and Cd²⁺ were used. 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 polyhedron with 14 vertices known as the sodalite cavity or β cage may be viewed as the principal

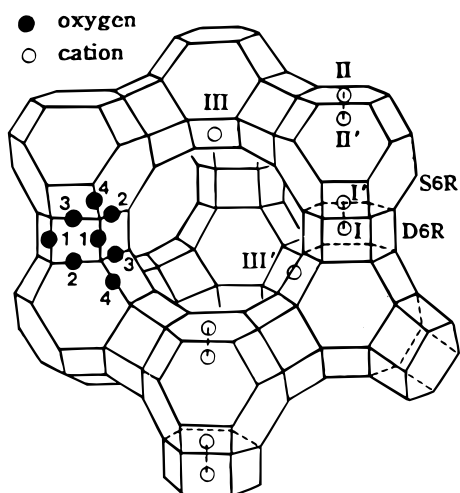


Figure 1. Stylized drawing of the framework structure of zeolite X. Near the center of each line segment is an oxygen atom. The different oxygen atoms are indicated by the numbers 1–4. Silicon and aluminum atoms alternate at the tetrahedral intersections, except that Si substitutes for about four of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

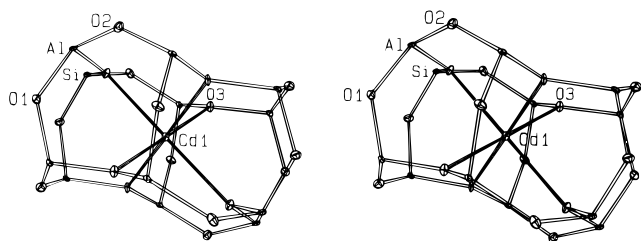


Figure 2. Stereoview of a double six-ring of $\text{Cd}_{46}\text{-X}\cdot 29.5\text{C}_2\text{H}_4$. The Cd^{2+} ion at Cd(1) is shown at site I. Ellipsoids of 20% probability are used.

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 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 six-rings from site I, II' inside the sodalite cavity near a single six-ring (S6R, shared by a β 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).^{22,23}

The Cd^{2+} ions are found at three different crystallographic sites. At sites I and I', 15.5 Cd^{2+} ions at Cd(1) and one Cd^{2+} ion at Cd(2) are found per unit cell, respectively (see Figures 2 and 3). Each of the 29.5 Cd^{2+} ions per unit cell at Cd(3) lies at site II, on a 3-fold axis in the supercage, close to three O(2) framework oxygens (see Figures 4, 5, and 6). These occupancy numbers differ from those in dehydrated $\text{Cd}_{46}\text{-X}$,¹⁴ $\text{Cd}_{46}\text{-X}\cdot 28\text{CO}$,¹⁵ and $\text{Cd}_{46}\text{-X}\cdot 28\text{C}_2\text{H}_2$ ¹⁶ (see Table 3).

Each Cd^{2+} ion at site I in $\text{Cd}_{46}\text{-X}\cdot 29.5\text{C}_2\text{H}_4$ coordinates to six O(3) framework oxygens. The octahedral Cd(1)–O(3)

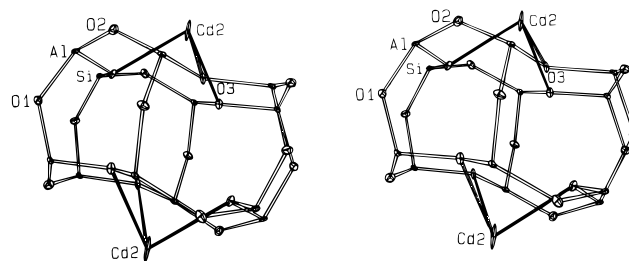


Figure 3. Stereoview of the less common D6R in $\text{Cd}_{46}\text{-X}\cdot 29.5\text{C}_2\text{H}_4$. The Cd^{2+} ions at Cd(2) (site I') are shown. The Cd(2)–Cd(2) repulsion (5.84 Å) is responsible for the large deviation of Cd(2) (1.57(2) Å) from the plane of its six-ring. Ellipsoids of 20% probability are used.

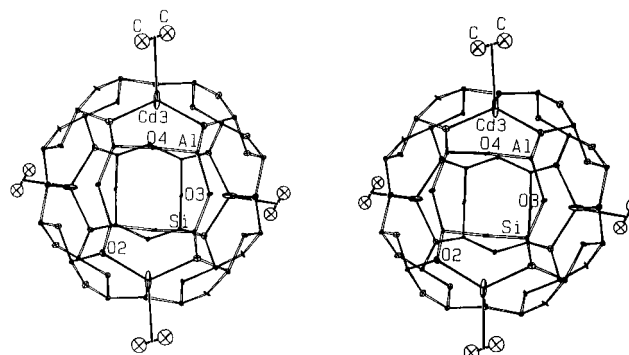


Figure 4. Stereoview of a sodalite cavity of dehydrated $\text{Cd}_{46}\text{-X}$ treated with C_2H_4 . Four Cd^{2+} ions lie at site II. Each coordinates to a C_2H_4 molecule. Ellipsoids of 20% probability are used.

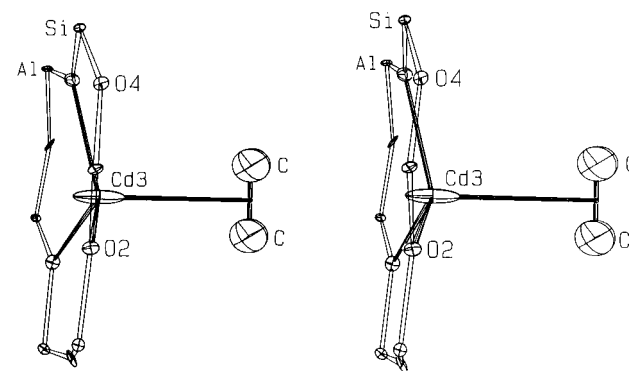


Figure 5. $\text{Cd}(\text{C}_2\text{H}_4)_2^{2+}$ complex on the inner surface of a supercage is shown in stereoview. The approximately tetrahedral coordination about Cd^{2+} can be seen. Ellipsoids of 20% probability are used.

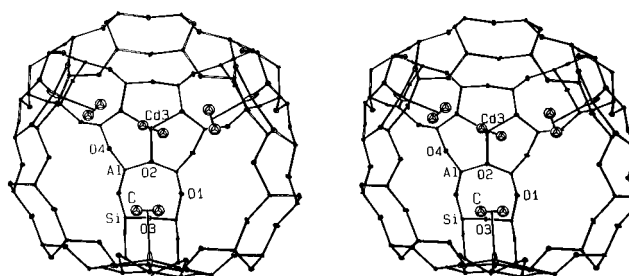


Figure 6. Stereoview of a supercage of $\text{Cd}_{46}\text{-X}\cdot 29.5\text{C}_2\text{H}_4$. Four Cd^{2+} ions at Cd(3) (site II) are shown. Each coordinates to an ethylene molecule. Ellipsoids of 20% probability are used.

distance, 2.350(6) Å, is just a little longer than the sum of the ionic radii of Cd^{2+} and O^{2-} 0.97 + 1.32 = 2.29 Å.²⁴ This Cd^{2+} –O distance is exactly the same as that in dehydrated $\text{Cd}_{46}\text{-X}$.¹⁴

TABLE 3: Structural Features of Cd₄₆-X and Its Sorption Complexes

	dehydrated	·28CO	·28C ₂ H ₂	·29.5C ₂ H ₄
no. of Cd ²⁺ ions at site I	16	13	13	15.5
no. of Cd ²⁺ ions at site I'	0	5	5	1
no. of Cd ²⁺ ions at site II	30	28	28	29.5
fractional coord of Cd ²⁺ at site II	0.2212(9)	0.2240(1)	0.2274(1)	0.2285(1)
deviation ^a of Cd ²⁺ from six-ring plane at O(2) (Å)	0.19(1)	0.33(1)	0.46(1)	0.50(1)
Cd ²⁺ -O(2) (Å)	2.16(1)	2.16(1)	2.19(1)	2.22(1)
O(2)-Cd-O(2) (deg)	119.2(5)	117.7(4)	115.7(3)	115.1(3)
reference	14	15	16	this work

^a A positive deviation indicates that the ion lies in the supercage. Numbers in parentheses are the esd's in the units of least significant digit given for the corresponding value.

One Cd²⁺ ion at site I' coordinates at 2.503(6) Å to three O(3) framework oxygens. The same distance, 2.502(8) Å, is found for a site-I' Cd²⁺ ion in the crystal structure of Cd₄₆-X·28C₂H₂.¹⁶ The shortest approach distance between sites I and I' is only 2.92 Å, so these cannot be simultaneously occupied because of electrostatic repulsion. Therefore, if a I site is occupied, the two adjacent I' sites (of the same D6R) cannot be.

The fractional occupancy observed at Cd(1) indicates the existence of at least two types of "unit cells" with regard to the double six-rings. Half of the unit cells would have a Cd(1) ion at the center of each of their 16 D6R's, and the remainder have only 15, with two Cd²⁺ ions at Cd(2) occupying sites I' outside the 16th, otherwise empty, D6R (see Figure 3). The 5.90 Å repulsive interaction between these two Cd(2) ions is responsible for the longer Cd-O distance (as compared to those for Cd(1) and Cd(3)) and the large deviation of Cd(2), 1.57(2) Å from the plane of its six-ring. Such large deviations of 2+ cations at site I' from the planes at their six-rings are also found in Cd₄₆-X·28CO (1.60 Å),¹⁵ Cd₄₆-X·28C₂H₂ (1.52 Å),¹⁶ and Mg₄₆-X (1.21 Å).²⁵

To coordinate to an ethylene molecule, each Cd²⁺ ion at Cd(3) has moved 0.50 - 0.19 = 0.31 Å (see Table 3) along its 3-fold axis toward the center of the supercage and away from its triad of three O(2) oxygens to a more tetrahedral coordination environment (considering ethylene to be monodentate). The deviation of Cd²⁺ ions from the six-ring plane at O(2) into the supercage is larger than those in any of the three structures Cd₄₆-X,¹⁴ Cd₄₆-X·CO,¹⁵ or Cd₄₆-X·C₂H₂.¹⁶ (see Table 3). The Cd(3)-O(2) bond length is also the longest (see Table 3). All of the O(2)-Cd(3)-O(2) angles in the three sorption structures of Cd₄₆-X (·CO, ·C₂H₂, and ·C₂H₄) are smaller than those in empty Cd₄₆-X (see Table 3).

In this structure, the mean values of the Si-O and Al-O bond lengths are only slightly longer than normal, 1.622 and 1.726 Å, respectively. The individual bond lengths, however, show marked variations: Si-O from 1.599(7) to 1.656(7) Å and Al-O from 1.691(7) to 1.761(7) 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, I', and II coordinate only to O(2) and O(3). Accordingly, the Al-O(2) and Al-O(3) distances are lengthened (see Table 2). This effect was seen before in empty Cd₄₆-X,¹⁴ Cd₄₆-X·28CO,¹⁵ Cd₄₆-X·28C₂H₂,¹⁶ Mn₄₆-X·30CO,¹⁷ Mn₄₆-X·30C₂H₄,¹⁷ Mg₄₆-X,²⁵ Ca₄₆-X,²⁵ and Ba₄₆-X.²⁵

One of the most interesting features of this structure is the binding of C₂H₄ molecules to Cd²⁺ ions. The ethylene molecules are located deep inside the supercage (see Figure 6). With 59 carbon atoms (29.5 molecules of C₂H₄) at Wyckoff position 96(g), the Cd²⁺-C₂H₄ interaction has symmetry *m*; that is, each C=C bond is normal to and bisected by a plane of symmetry which contains a 3-fold axis (and hence a Cd(3) ion),

TABLE 4: Comparison of Ethylene-Cation Approach Distances in Zeolites A and X

zeolites	M-C (Å)	cation radius (Å) ^a	effective ethylene radius (Å)	ref
Ag ₁₂ -A·3.6C ₂ H ₄ ^b	2.54(8)	1.26	1.28	9
Cd ₆ -A·4C ₂ H ₄	2.67(6)	0.97	1.70	10
Cd ₄₆ -X·29.5C ₂ H ₄	2.70(4)	0.97	1.73	this work
Co ₄ Na ₄ -A·4C ₂ H ₄	2.51(6)	0.72	1.79	8
Ca ₆ -A·4C ₂ H ₄	2.87(5)	0.99	1.88	27
Mn ₄₆ -X·30C ₂ H ₄	2.74(6)	0.80	1.94	17

^a Reference 24. ^b Nonintegral because some Ag⁺ ions were reduced. Others complex to H₂O in the sodalite unit.

so that both carbons are equidistant from Cd²⁺. However, the center of the C=C bond does not lie on the 3-fold axis. It is displaced from it by 0.36 Å.

The C=C distance is 1.26(5) Å. For comparison, the C=C bond length in ethylene gas is 1.344 Å, while in nonzeolitic transition-metal complexes, a broad range of C=C distances (from 1.354(15) to 1.46(2) Å) can be seen.²⁶ The C=C distances in other zeolite structures also range widely (1.21-1.11) Å in Co₄Na₄-A·4C₂H₄,⁸ 1.19(12) Å in Ag₁₂-A·3.6C₂H₄,⁹ 1.48(7) Å in Ca₆-A·4C₂H₄,²⁷ due to the combined effects of disorder and high thermal motion of the carbon atoms. None of the C=C distances in zeolite complexes have been determined with sufficient precision to detect a change upon sorption.

The bonding between the Cd²⁺ ion and ethylene is usually described in terms of the Chatt-Dewar model.²⁸ A σ component arises from the overlap of a filled ethylene orbital and a vacant Cd²⁺ 5s orbital, and a π component occurs by the overlap of the filled 4d orbitals of Cd²⁺ with the vacant antibonding π^* orbital of ethylene. Due to the latter back-donation interaction, the C=C bond order may be diminished somewhat. The difference between cadmium and silver in their ability to back-donate 4d electrons to the π^* orbital of ethylene can be attributed to the difference in their ionic radii: Cd²⁺ has a radius of 0.98 Å compared to 1.26 Å for Ag⁺. The filled 4d orbitals of Cd²⁺ therefore do not reach as far out in space as those of Ag⁺, so Cd²⁺ cannot back-bond as effectively to ethylene. Therefore, the Cd²⁺-C distances of 2.67(6) Å in Cd₆-A·4C₂H₄¹⁰ and 2.70(4) Å in Cd₄₆-X·29.5C₂H₄ (this work) are longer than the Ag⁺-C distance of 2.54(8) Å in Ag₁₂-A·3.6C₂H₄.⁹ Yet the back-bonding remains sufficient to prevent free rotation.¹⁸

The present structure is very similar to that of an ethylene sorption complex of Mn₄₆-X.¹⁷ In that complex, each of the 30 Mn²⁺ ions at site II associates with one C₂H₄ molecule in the supercage. Each ion at site II has a geometry between trigonal pyramidal and tetrahedral and is 2.12(2) Å from three framework oxygens and 2.74(6) Å from a carbon atom of a C₂H₄ molecule.

In both Cd₄₆-X·28CO¹⁵ and Cd₄₆-X·28C₂H₂,¹⁶ it appears that the movement of site II cations away from the sodalite

cavities upon complexation has allowed site I' to become occupied. Some Cd²⁺ ions from both sites I and II relocated to site I'. Perhaps because the Cd²⁺ ions at site II coordinate somewhat more strongly to C₂H₄ than to C₂H₂ or CO (see Table 3), more of them do so, and fewer Cd²⁺ ions remain to relocate to site I'.

The Cd²⁺-C distances are 2.70(4) Å in length, a value much greater than those usually found in neutral metal ethylene π complexes, and, accordingly, this metal ion-alkene interaction is considered weak. (Neutral metal to ethylene carbon distances (metal = Co, Ni, Cu, Nb, Ru, Rh, Ta, W, Ir, and Pt) range from 1.98(2) to 2.20(4) Å in a series of several inorganic compounds.²⁹) Essentially, the same long Cd-C distance, and the same mode of attachment, is observed in the structure of Cd₆-A·4C₂H₄¹⁰ (2.67(6) Å) (see Table 4). For comparison, the corresponding M-C distances in other intrazeolitic metal ethylene complexes are given in Table 4. No other (no nonzeolitic) examples of π -bonded cadmium(II) alkene structures have been reported.

In summary, Cd²⁺ ions occupy sites I, I', and II. Each of the 29.5 ethylene molecules sorbed per unit cell coordinates to a Cd²⁺ ion in the supercage. From this and previous crystallographic studies of the carbon monoxide and acetylene complexes of transition-metal-exchanged zeolite X, two conclusions may be reached: (1) the sorbed molecules interact only with the site-II metal ions and (2) because the M²⁺-C approach distances are long, these interactions are weak.

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Supporting Information Available: Tables of observed and calculated structure factors with esd's (9 pages). Ordering information is given on any current masthead page.

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