

Crystal Structure of a Zinc Sorption Complex of Cd^{2+} -Exchanged Zeolite X Containing Tetrahedral $\text{Cd}^{2+}_4(\mu_3\text{-Zn}^0\text{Cd}^{2+}\text{Zn}^0)_4$ Clusters

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Received: March 24, 1999; In Final Form: May 20, 1999

The sorption of Zn vapor at 480 °C onto fully dehydrated fully Cd^{2+} -exchanged zeolite X ($\text{Cd}_{46}\text{Si}_{100}\text{Al}_{92}\text{O}_{384}$ per unit cell) has been studied at 23 °C by single-crystal X-ray diffraction in the cubic space group $Fd\bar{3}$ ($a_0 = 24.895(3)$ Å). In this structure, $\text{Cd}_{46}\text{Si}_{100}\text{Al}_{92}\text{O}_{384}\cdot 20\text{Zn}$, Cd^{2+} ions are found at five nonequivalent sites, redistributed significantly from 16, 0, 30, 0, 0 in dehydrated $\text{Cd}_{46}\text{-X}$ to 12, 8, 12, 6, 8 (best integers) at sites I, I', II, III', and another III', respectively. The 8 Cd^{2+} ions at site I' and 8 of the 12 Cd^{2+} ions at site II have captured 16 Zn atoms to form two $\text{Cd}^{2+}_4(\mu_3\text{-Zn}^0\text{Cd}^{2+}\text{Zn}^0)_4$ clusters per unit cell. The remaining four Cd^{2+} ions at site II have captured the remaining (about four) Zn atoms. Each $\text{Cd}^{2+}_4(\mu_3\text{-Zn}^0\text{Cd}^{2+}\text{Zn}^0)_4$ cluster has at its center interpenetrating tetrahedra of $(\text{Cd}^{2+})_4$ and $(\text{Zn}^0)_4$ in the sodalite unit, with four terminal $\text{Cd}^{2+}\text{-Zn}^0$ groups extending radially into the supercage from each of the above Zn^0 atoms; Cd^{2+} ions and Zn^0 atoms alternate throughout. The central four Zn^0 atoms form a tetrahedral Zn_4^0 cluster with $\text{Zn}\text{-Zn} = 2.88(4)$ Å, somewhat longer than the 2.66 Å distance in Zn metal, due perhaps to delocalization of bonding density to adjacent Cd^{2+} ions. In each $\text{Cd}^{2+}_4(\mu_3\text{-Zn}^0\text{Cd}^{2+}\text{Zn}^0)_4$ cluster, each sodalite unit Cd^{2+} ion has a distorted octahedral environment, 2.566(11) Å to three framework oxygens and 2.410(11) Å to three Zn atoms; each Cd^{2+} ion at site II coordinates equatorially to three framework oxygens at 2.225(8) Å and axially to two Zn atoms at 2.408(23) Å and 1.97(5) Å, respectively. Each sodalite unit Zn atom coordinates tetrahedrally to four Cd^{2+} ions; each terminal Zn atom interacts only with one Cd^{2+} ion. Surprisingly, no Cd^{2+} ions have been reduced by Zn atoms; all Cd^{2+} ions are at reasonable bonding distances to framework oxygens, and all Zn atoms are far from framework oxygens. About 12 Cd^{2+} ions remained at site I upon Zn sorption; each coordinates octahedrally to six framework oxygens at 2.430(10) Å. About $6 + 8 = 14$ Cd^{2+} ions have relocated to two III' sites, 2.46(5) Å and 2.38(3) Å, respectively, from framework oxygens.

1. Introduction

The exchangeable cations in zeolites have received a great deal of attention in the scientific literature. The thermal stability, sorption parameters, and catalytic properties of zeolites all depend on the type and number of exchangeable cations and their distribution over the available sites.

The Na^+ ions in zeolite X can be completely and stoichiometrically exchanged by group IIA metal cations.^{1–3} Among the dipositive transition metal cations, however, only $(\text{Mn}^{2+})^4$ and $(\text{Cd}^{2+})^5$ have been so simply exchanged into zeolite X. More complex outcomes are seen when aqueous ion exchange is attempted with (Co^{2+}) ,⁶ (Pb^{2+}) ,⁷ and (Zn^{2+}) ,^{8–10} to cite three examples. Protons from the hydrolysis of these cations can attack zeolite frameworks, and hydroxide ions from this same hydrolysis may accompany cations into the zeolitic structure. When extensive ion exchange of Cu^{2+} or Hg^{2+} into zeolite X is attempted from aqueous solution, the former causes severe crystal damage and the latter destroys the zeolite.¹¹

The complete ion exchange of metal ions into zeolites has been accomplished by chemical vapor deposition and reaction (CVDR) of metals with appropriate reduction potential. In contrast to conventional ion exchange methods such as exchange with aqueous solution^{1–14} and solid-state ion exchange,¹⁵ CVDR works under rigorously anhydrous conditions. When zeolites containing alkali metal cations are exposed to an alkali metal vapor, sorption,^{16–22} and sometimes redox reaction,^{23–27} can occur. Heo et al. has successfully introduced indium cations

into zeolite A by reacting In metal vapor with TI-A.²⁸ Recently, the redox reaction of zeolite H–Y with zinc metal vapor has been used to ion-exchange zinc cations into zeolite Y.^{29–31}

In this work, Zn vapor was introduced to fully dehydrated $\text{Cd}_{46}\text{-X}$ with the hope of preparing stoichiometrically Zn^{2+} -exchanged zeolite X. This had not been possible by aqueous methods because of overexchange.^{8,10} For one of the crystals, the reaction did not go beyond an initial stage. Its structure is reported here.

2. Experimental Section

2.1. Crystal Preparation. Large single crystals of sodium zeolite X of stoichiometry $\text{Na}_{92}\text{Si}_{100}\text{Al}_{92}\text{O}_{384}$ per unit cell were prepared in Leningrad, now St. Petersburg, Russia.³² One of these, a colorless octahedron about 0.12 mm in cross section, was lodged in a fine Pyrex capillary. Aqueous 0.05 M $\text{Cd}(\text{NO}_3)_2$ (Fisher Scientific, Certified, alkalis and earths 0.10%, Zn 0.05%, Pb 0.003%, Cu 0.0007%, Fe 0.0005%) was allowed to flow past the crystal at a velocity of 2.0 cm/s for 2 days.⁵ The crystal was transferred to another capillary that contained small particles of Zn metal (Baker Analyzed Reagent, 99.9%, Pb 0.010%, Fe 0.003%) near its tip. The capillary containing the crystal and Zn metal was attached to a vacuum system. Both were cautiously dehydrated by gradually increasing the temperature (ca. 15 °C/h) to 480 °C at a pressure of 1×10^{-5} Torr. After the system was maintained at these conditions for 8 days as Zn vapor (vapor pressure = 1 Torr)³³ flowed past the crystal

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

atom	wyc. pos.	site	x	y	z	U_{11} or U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	occupancy ^b	
												varied	fixed
Si	96(g)		-532(1 ^c)	1233(2 ^c)	355(1 ^c)	203(19)	138(17)	164(19)	7(16)	11(15)	-32(17)		96 ^d
Al	96(g)		-535(1 ^c)	363(1 ^c)	1229(2 ^c)	158(19)	110(18)	87(18)	25(15)	-3(16)	-38(16)		96 ^d
O(1)	96(g)		-1093(4)	-4(4)	1076(4)	383(63)	292(56)	305(58)	-94(48)	-20(44)	-127(46)		96 ^d
O(2)	96(g)		-31(4)	-36(4)	1444(4)	228(49)	241(49)	228(47)	167(42)	-55(42)	-91(42)		96 ^d
O(3)	96(g)		-318(4)	662(4)	643(4)	282(58)	439(68)	484(70)	192(52)	157(52)	126(54)		96 ^d
O(4)	96(g)		-676(4)	804(4)	1705(4)	392(60)	225(52)	250(53)	-12(46)	25(47)	-150(42)		96 ^d
Cd(I)	16(c)	I	0	0	0	182(11)	182(11)	182(11)	18(9)	18(9)	18(9)	11.5(2)	12 ^e
Cd(I')	32(e)	I'	709(2)	709(2)	709(2)	362(28)	362(28)	362(28)	73(22)	73(22)	73(22)	8.3(2)	8 ^e
Cd(II)	32(e)	II	2217(1)	2217(1)	2217(1)	299(20)	299(20)	299(20)	150(16)	150(16)	150(16)	12.3(2)	12 ^e
Cd(III')	96(g)	III'	2811(32)	1803(19)	4182(12)	1544(286)						6.5(11)	6 ^e
Cd(III'')	96(g)	III''	2439(18)	1737(12)	4183(12)	1132(159)						8.4(10)	8 ^e
Zn(II')	32(e)	II'	1659(5)	1659(5)	1659(5)	1633(121)	1633(121)	1633(121)	-183(88)	-183(88)	-183(88)	11.3(5)	12 ^e
Zn(II)	32(e)	II	2674(12)	2674(12)	2674(12)	2087(271)	2087(271)	2087(271)	1005(250)	1005(250)	1005(250)	8.5(6)	8 ^e

^a Positional and thermal parameters are given $\times 10^4$. Numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding parameter. The anisotropic temperature factor = $\exp[-2\pi^2 a^{-2}(h^2 U_{11} + k^2 U_{22} + l^2 U_{33} + 2hku_{12} + 2hlu_{13} + 2klu_{23})]$. ^b Occupancy factors are given as the number of atoms or ions per unit cell. ^c The esd's of the coordinates of Si and Al are all approximately 1.4×10^{-4} . ^d This occupancy was fixed in least-squares refinement. ^e These integral occupancies which sum to 46 Cd²⁺ ions per unit cell are used to facilitate the discussion.

into a dynamic vacuum, the hot contiguous downstream lengths of the vacuum system, including a sequential U-tube of beads of zeolite 3A fully activated in situ, were cooled to ambient temperature to prevent the movement of water molecules from more distant parts of the vacuum system to the crystal. Then, the crystal was slowly cooled to 24 °C in 24 h. The resulting lustrous black crystal was sealed off in its capillary by torch. No deposition of Zn was observed on the cooler glass downstream from the crystal, indicating that the crystal may not have been exposed to an excess of Zn.

2.2. X-ray Data Collection. The cubic space group $Fd\bar{3}$ was used throughout this work. It was justified by its reflection conditions (hkl : $h + k, k + l, l + h = 2n$; $0kl$: $k + l = 4n$); however, the intensity inequality observed for the hkl and kh reflections was not as significant for this crystal as it was in numerous previous determinations using crystals from the same batch.²⁻⁵ Generally, crystals subjected to gentle chemical treatment retain this intensity inequality. This space group requires that the Si and Al atoms alternate in obedience of Loewenstein's rule;³⁴ about 4% of the Al sites are occupied by Si atoms. Molybdenum K α radiation was used ($K\alpha_1 = 0.70930$ Å; $K\alpha_2 = 0.71359$ Å).

The unit cell constant at 23 °C, $a_0 = 24.895(3)$ Å, was determined by least-squares refinement of 34 intense reflections for which $10^\circ < 2\theta < 26^\circ$. All unique reflections in the positive octant of an F-centered unit cell for which $3^\circ < 2\theta < 50^\circ$ were recorded at 23 °C.

Of the 3675 reflections gathered, 1154 were unique; $F_o > 4\sigma(F_o)$ for 529 of these.

3. Structure Determination

Full-matrix least-squares refinement³⁵ was done on F^2 using all unique reflections. It was initiated with the atomic parameters of the framework atoms [Si, Al, O(1), O(2), O(3), and O(4)] from Olson's determination of the structure of dehydrated Na-X.³⁶ Fixed weights of $a = 0.10$ and $b = 0$ were used initially; the final weights were assigned using the formula $w = q/[\sigma^2(F_o^2) + (aP)^2 + bP + d + e \sin(\theta)]$, where $P = fF_o^2 + (1 - f)F_c^2$, to give $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$, with a and b as refined parameters. $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma F_o$ was calculated using the 529 reflections for which $F_o > 4\sigma(F_o)$ and $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma(F_o^2)^2\}^{1/2}$ is based on F_o^2 and was calculated using all 1154 unique reflections examined.

Isotropic refinement of the framework atoms converged to $R_1/wR_2 = 0.49/0.83$. A difference Fourier function revealed three large peaks at (0.0, 0.0, 0.0), (0.220, 0.220, 0.220), and (0.071, 0.071, 0.071), all with reasonable Cd-O distances to framework oxygens. Isotropic refinement treating them as Cd²⁺ ions at Cd(I), Cd(II), and Cd(I'), respectively, converged quickly to $R_1/wR_2 = 0.13/0.36$.

An ensuing difference Fourier function revealed a strong peak at (0.167, 0.167, 0.167), approximately 2.41 Å from both Cd(I) and Cd(II'), but not close to framework oxygens. It was refined as Zn(II') to $R_1/wR_2 = 0.12/0.33$.

Another strong peak was found at (0.254, 0.171, 0.427), 2.4 Å from a framework oxygen in the supercage. Refinement including it as Cd(III*) led to $R_1/wR_2 = 0.11/0.28$. Further refinement with all atoms anisotropic converged to $R_1/wR_2 = 0.091/0.26$.

The next difference Fourier function revealed another strong peak at (0.250, 0.250, 0.250) that refined anisotropically as Zn(2) to $R_1/wR_2 = 0.080/0.22$.

The principal mean square atomic displacements at the Cd(III*) position were 1.007, 0.239, and 0.077 Å², unreasonably large in one dimension, suggesting that it should be split into two positions. Refinement with the two suggested positions, Cd(III'), (0.268, 0.182, 0.418), and Cd(III''), (0.239, 0.169, 0.433), converged to the final $R_1/wR_2 = 0.081/0.22$.

In the final cycle of least-squares refinement, all shifts in atomic parameters were less than 0.1% of their corresponding standard deviations. The final difference Fourier function was almost featureless, indicating that all atoms were accounted for. The largest peak, 1.5 eÅ⁻³ at (0.245, 0.245, 0.245), between Cd(II) and Zn(II) and too close to both but not close to other atoms, refined to an insignificant occupancy and was not included in the final refinement. The goodness-of-fit = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2} = 0.945$; the number of unique reflections, n , is 1154, and the number of parameters, p , is 84. Atomic scattering factors for Si, Al, O, Cd, and Zn were used.³⁷ All scattering factors were modified to account for anomalous dispersion.³⁸ The final structural parameters are presented in Table 1, and selected interatomic distances and angles are in Table 2.

4. Discussion

4.1. Structure of Zeolite X. Zeolite X is a synthetic counterpart of the naturally occurring mineral faujasite (see Figure 1). The 14-hedron with 24 vertexes known as the sodalite

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

Si—O(1)	1.660(9)	O(1)—Si—O(2)	111.3(5)
Si—O(2)	1.650(9)	O(1)—Si—O(3)	108.0(6)
Si—O(3)	1.680(10)	O(1)—Si—O(4)	109.3(5)
Si—O(4)	1.631(9)	O(2)—Si—O(3)	106.4(5)
mean Si—O	1.655	O(2)—Si—O(4)	109.4(5)
		O(3)—Si—O(4)	112.5(5)
Al—O(1)	1.695(9)	O(1)—Al—O(2)	111.7(5)
Al—O(2)	1.687(9)	O(1)—Al—O(3)	107.1(5)
Al—O(3)	1.723(10)	O(1)—Al—O(4)	109.7(5)
Al—O(4)	1.653(9)	O(2)—Al—O(3)	106.9(5)
mean Al—O	1.690	O(2)—Al—O(4)	108.8(5)
		O(3)—Al—O(4)	112.8(5)
Cd(I)—O(3)	2.430(10)	Si—O(1)—Al	129.8(6)
Cd(I')—O(3)	2.566(11)	Si—O(2)—Al	140.6(6)
Cd(II)—O(2)	2.225(8)	Si—O(3)—Al	128.9(6)
Cd(III')—O(1)	2.46(5)	Si—O(4)—Al	154.7(7)
Cd(III'')—O(4)	3.05(6)	O(3)—Cd(I)—O(3)	89.4(3), 90.6(3)
Cd(III''')—O(1)	2.38(3)	O(3)—Cd(I')—O(3)	107.8(7)
Cd(III''')—O(4)	3.319(6)	O(2)—Cd(II)—O(2)	119.19(9)
	3.400(7)	O(2)—Cd(II)—Zn(II)	95.2(3)
Cd(I')—Zn(II')	2.410(11)	O(2)—Cd(II)—Zn(II')	84.8(3)
Cd(II)—Zn(II')	2.408(23)	Zn(II')—Cd(I')—Zn(II')	73.3(8)
Cd(II)—Zn(II)	1.97(5)	Cd(I')—Zn(II')—Cd(I')	104.5(6)
Zn(II')—Zn(II')	2.88(4)	Cd(II)—Zn(II')—Cd(I')	114.1(5)
		Zn(II')—Cd(II)—Zn(II)	180 ^b

^a Numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding parameter. ^b Exactly, by symmetry.

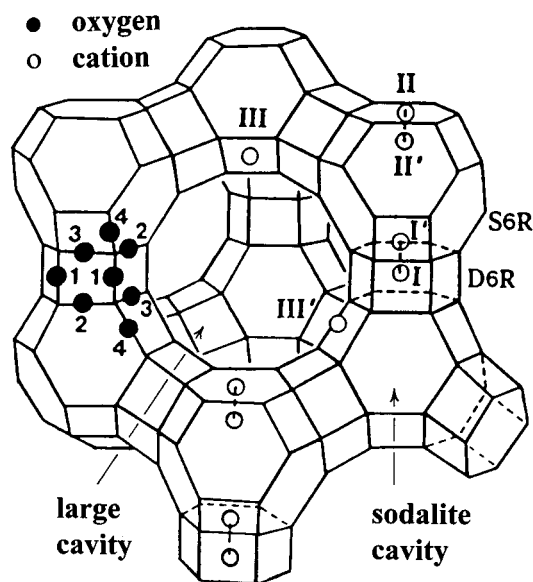


Figure 1. Stylized drawing of the framework structure of zeolite X. Near the center of the each line segment is an oxygen atom. The different oxygen atoms are indicated by the numbers 1–4. Silicon and aluminum alternate at the tetrahedral interactions, except that Si substitutes for about 4% of the Al's.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

cavity or β cage may be viewed as its principal building block. These β cages are connected tetrahedrally at six-rings by bridging oxygens to give double six-rings (D6R's, hexagonal prisms), and concomitantly to give an interconnected set of even larger cavities (supercages, α cages) 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 midway between each pair of Si and Al atoms, but are displaced from those points to give near tetrahedral angles about Si and Al. Single six-rings (S6R's) are shared by sodalite and supercages and may be viewed as entrances to the

sodalite units. Each unit cell has 8 sodalite units, 8 supercages, 16 D6R's, 16 12-rings, and 32 S6R's.

Exchangeable cations that balance the negative charge of the aluminosilicate framework are found within the zeolite's cavities. They are usually found at the following general sites shown in Figure 1: I at the center of a D6R, I' in the sodalite cavity on the opposite side of one of the D6R's six-rings from site I, II' inside the sodalite cavity near a S6R, II in the supercage adjacent to a S6R, III in the supercage opposite a four-ring between two 12-rings, and III' somewhat or substantially distant from III but otherwise near the inner walls of the supercage or the edges of 12-rings.

4.2. Structure of Cd₄₆-X·20Zn. The mean values of the Si—O and Al—O bond lengths, 1.655 and 1.690 Å, respectively, are somewhat different, partially justifying the use of the space group *Fd* $\bar{3}$.

In dehydrated Cd₄₆-X,⁵ Cd²⁺ ions occupy only two sites, each with high occupancy. Sixteen Cd²⁺ ions fill site I at the centers of the D6R's. The remaining 30 Cd²⁺ ions nearly fill site II in the supercage; each of these is slightly recessed (0.19 Å) into the supercage from its three-oxygen plane. However, upon the sorption of zinc vapor, the Cd²⁺ ions have sharply redistributed themselves within the zeolite structure. Only about 24 of the 46 Cd²⁺ ions remained at sites I and II, about 12 at each. The remaining 22 Cd²⁺ ions moved to new cation sites, about eight to site I' and six and eight to two independent III' sites. The sodalite units remain full or nearly so by the formula (no. at I) + (no. at I')/2 \leq 16, which is required to avoid the impossibly short I—I' distance.

The Cd²⁺—O²⁻ bond lengths observed for the Cd²⁺ ions at sites I, I', and II (see Table 2) are very similar to those in the acetylene sorption complex of Cd₄₆-X, Cd₄₆Si₁₀₀Al₉₂O₃₈₄·28C₂H₂,³⁹ 2.388(8), 2.503(8), and 2.192(8) Å, respectively. They are all a little longer here, perhaps because the Zn⁰ atoms have donated some electron density to Cd²⁺. These distances have been discussed previously.³⁹ As before, the long Cd(I')—O(3) distance is attributed to Cd(I')—Cd(I') repulsion through the D6R's that the Cd(I') ions must share. Upon C₂H₂ sorption, however, many fewer Cd²⁺ ions, only five per unit cell, relocated from the positions they occupied in empty Cd₄₆-X;⁵ these all moved to site I'.

4.3. Cd²⁺₄(μ_3 -Zn⁰Cd²⁺Zn⁰)₄ Clusters. The 8 Cd²⁺ ions at site I', 8 of the 12 Cd²⁺ ions at site II, the 8 Zn atoms at site II, and 8 of the 12 Zn atoms at site II' form two Cd²⁺₄(μ_3 -Zn⁰Cd²⁺Zn⁰)₄ clusters per unit cell (see Figure 2). The refined occupancies indicate that the above statement should more accurately be "the 8.3 Cd²⁺ ions at site I', 8.3 of the 12.3 Cd²⁺ ions at site II, the 8.3 Zn atoms at site II, and 8.3 of the 11.3 Zn atoms at site II', form 2.1 Cd²⁺₄(μ_3 -Zn⁰Cd²⁺Zn⁰)₄ clusters per unit cell". At the heart of this cluster is a tetrahedron of four Zn⁰ atoms with a Zn(II')—Zn(II') distance of 2.88(4) Å, somewhat longer than the 2.66 Å Zn—Zn bond length in Zn metal⁴² likely due to the delocalization of bonding density to the adjacent Cd²⁺ ions but still within bonding distance. For the same reason, the Cd(II)—O(2) bond length increased somewhat from 2.16(1) Å in empty Cd₄₆-X to 2.225(8) Å upon sorption. These distances are both shorter than the sum of the conventional radii⁴³ of Cd²⁺ and O²⁻, 0.97 Å + 1.32 Å = 2.29 Å.

In each Cd²⁺₄(μ_3 -Zn⁰Cd²⁺Zn⁰)₄ cluster, each Cd²⁺ ion at site I' has a distorted octahedral environment, 2.566(11) Å to three framework oxygens and 2.410(11) Å to three Zn atoms. Each Cd²⁺ ion at site II coordinates equatorially to three framework oxygens at 2.225(8) Å and axially to Zn(II') at 2.408(23) Å

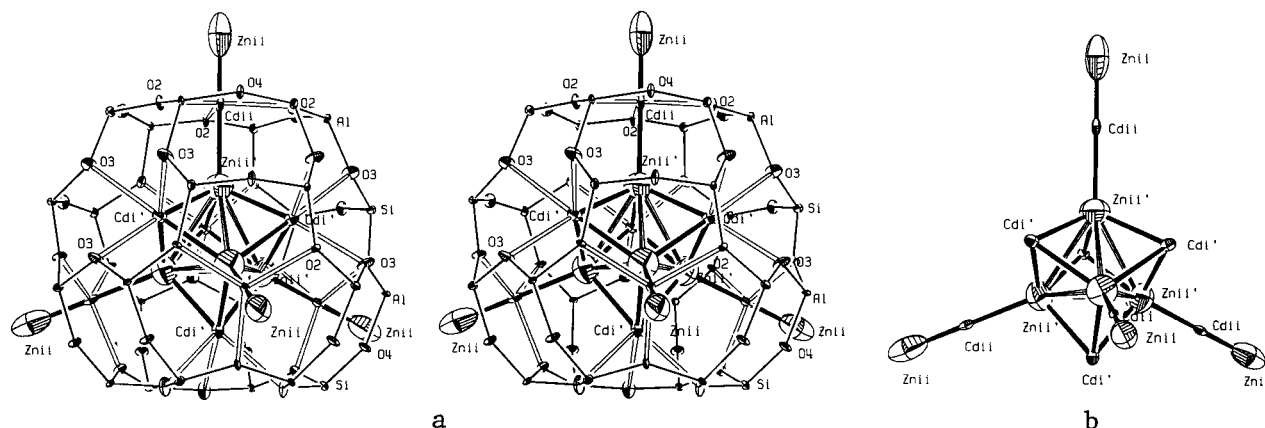


Figure 2. (a) Stereoview of a $\text{Cd}^{2+}_4(\mu_3\text{-Zn}^0\text{Cd}^{2+}\text{Zn}^0)_4$ cluster in the sodalite cavity. A tetrahedral Zn_4^0 cluster is at its center. Each ion at Cd(I') coordinates to three O(3) framework oxygens and three Zn(II') atoms; each ion at Cd(II) coordinates equatorially to three O(2) framework oxygens and axially to two Zn atoms at Zn(II') and Zn(II) . Zn atoms at Zn(II) coordinate to four Cd^{2+} ions tetrahedrally; each atom at Zn(II) interacts only with one Cd^{2+} ion at Cd(II) . This and subsequent figures were drawn with thermal ellipsoids of 20% probability using the program Ortep3.^{40,41} (b) The tetrahedral $\text{Cd}^{2+}_4(\mu_3\text{-Zn}^0\text{Cd}^{2+}\text{Zn}^0)_4$ cluster.

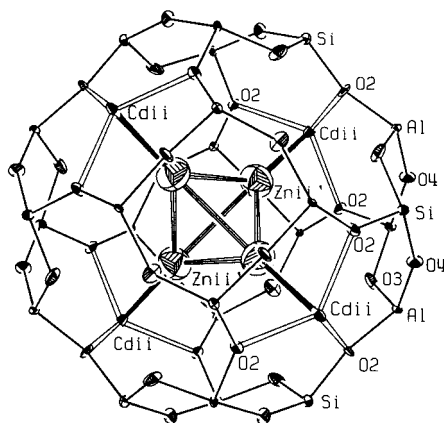


Figure 3. A possible $\text{Cd}^{2+}_4\text{Zn}_4$ cluster in a sodalite cavity. Smaller clusters using these positions, such as $\text{cyclo-(Cd}^{2+})_3(\text{Zn}^0)_3$, $\text{Cd}^{2+}_3(\text{Zn}^0)_3$, and $\text{Cd}^{2+}_2\text{Zn}_2$, are also possible. The refined occupancies suggest that not all four Cd^{2+} ions have captured a Zn atom.

and Zn(II) at 1.97(5) Å. Each Zn(II') atom coordinates tetrahedrally to four Cd^{2+} ions, but each atom at Zn(II) is terminal; it interacts only with a site-II Cd^{2+} ion.

The remaining four Cd^{2+} ions at site II and four Zn atoms at site I' could possibly form a $\text{Cd}^{2+}_4\text{Zn}_4$ cluster (see Figure 3), one per unit cell. They could also form smaller clusters such as $\text{cyclo-(Cd}^{2+})_3(\text{Zn}^0)_3$, 4/3 per unit cell, $\text{Cd}^{2+}_3(\text{Zn}^0)_3$, two per unit cell, or $\text{Cd}^{2+}_2\text{Zn}_2$, four per unit cell, using the positions shown in Figure 3. The Zn–Zn distance, 2.88(4) Å, indicates the possibility of bonding as discussed in the previous paragraph. This bond length should be somewhat inaccurate because both the Zn(II') and Cd(II) positions used best describe those in the $\text{Cd}^{2+}_4(\mu_3\text{-Zn}^0\text{Cd}^{2+}\text{Zn}^0)_4$ cluster.

An alternative distribution of Cd^{2+} ions and Zn^0 atoms would involve three $\text{Cd}^{2+}_4\text{Zn}_4$ clusters as shown in Figure 3, only two of which are further surrounded by four Zn atoms at Zn(II) (shown in Figure 2b). Eight Cd^{2+} ions (at site I') distributed among the five remaining sodalite units per unit cell would each coordinate only to three framework oxygens. This arrangement provides no apparent justification for the shift of Cd^{2+} ions from site I, its preferred site in empty $\text{Cd}_{46}\text{-X}$, to site I'. It is considered unlikely.

Because Zn(II') has a large thermal parameter and is an average of two nonequivalent Zn^0 positions, an attempt was made to resolve it. Refinement with variable occupancies at two

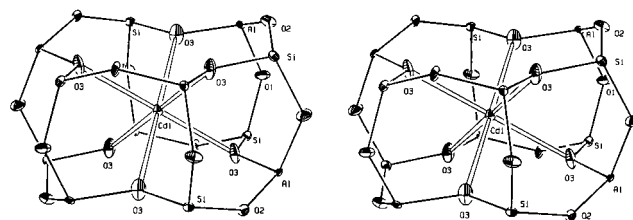


Figure 4. Stereoview of a D6R containing a Cd^{2+} ion at Cd(I) . Each Cd^{2+} ion coordinates octahedrally to six O(3) framework oxygens.

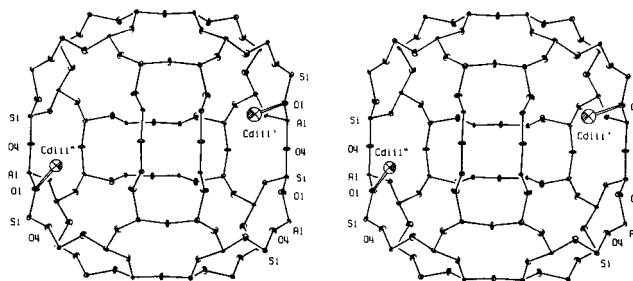


Figure 5. Stereoview of a supercage. The Cd^{2+} ions at Cd(III') and Cd(III'') each bond to one O(1) framework oxygen.

positions did not converge. Refinement with fixed occupancies did not yield sensible thermal parameters. Accordingly, Zn(II') was left unresolved.

The large thermal parameters of the atoms at Zn(II) can be understood because each bonds only to one Cd^{2+} ion. For the same reason, the Cd^{2+} –Zn distances are observed to be very short, 1.97(5) Å as compared to the sum of radii of Cd^{2+} and Zn^0 , 0.97 Å⁴³ + 1.33 Å⁴² = 2.30 Å. These Cd^{2+} –Zn bond lengths may be somewhat foreshortened due to the effect of thermal motion. The Cd(I')-Zn(II') and Cd(II)-Zn(II') distances are 2.410(11) Å and 2.408(23) Å, respectively, in better agreement with the sum of the radii of Cd^{2+} and Zn^0 .

4.4. Nonclustering Cd^{2+} Ions. The Cd^{2+} ions at Cd(I) are only 3.057(8) Å from those at Cd(I') . If site I is occupied, the two adjacent I' sites should not be, to avoid the electrostatic repulsion.³⁹ Each of the eight Cd^{2+} ions at Cd(I') must therefore occupy one of the eight I' sites outside the four remaining empty D6R's per unit cell. The 12 Cd^{2+} ions at Cd(I) each coordinate octahedrally to six O(3) framework oxygens (see Figure 4); these and the eight Cd^{2+} ions at Cd(I') effectively fill sites I and I'. The Cd(I)-O(3) distance, 2.430(10) Å, increased slightly as compared to 2.35(1) Å in $\text{Cd}_{46}\text{-X}$. About 14 Cd^{2+} ions are

found at two general positions, sites III', with occupancies 6 and 8, and coordinate to framework oxygen O(1) at 2.46(5) and 2.38(3) Å, respectively (see Figure 5).

5. Conclusion

It is surprising that the sorbed Zn did not react with the Cd²⁺ ions in this structure; the aqueous \mathcal{E}^0 for this reaction is +0.36 V.⁴⁴ This \mathcal{E}^0 is usually a relatively reliable basis for judgment even within a dehydrated zeolite, perhaps because the ligands in both cases are largely covalent O²⁻. In a more exhaustive treatment of Cd₄₆-X with Zn vapor, also at 480 °C, where a much greater quantity of Zn vapor was allowed to pass over a single crystal of Cd₄₆-X, all Cd²⁺ ions were reduced by Zn atoms.¹¹ Apparently the first Zn⁰ atoms to enter Cd₄₆-X form clusters without redox reaction. Further sorbed Zn⁰ then reacts with these clusters and the remaining Cd²⁺ ions to give Zn²⁺ ions and Cd⁰ atoms that leave the zeolite at 480 °C as Cd(g).

Supporting Information Available: Tables of observed and calculated structure factors squared with esd's. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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