

Crystal Structure of a Cadmium Sorption Complex of Dehydrated Fully Cd²⁺-Exchanged Zeolite X Containing Cd²⁺, Cd⁺, and Cd⁰

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A single crystal of fully dehydrated fully Cd²⁺-exchanged zeolite X, Cd₄₆Si₁₀₀Al₉₂O₃₈₄ per unit cell, was exposed at 320 °C to 0.005 Torr of Cd vapor for 9 days. The resultant crystal, Cd₆₈Si₁₀₀Al₉₂O₃₈₄ per unit cell [*a* = 24.953(6) Å], was determined by single-crystal X-ray diffraction techniques in the cubic space group *Fd3m* at 21(1) °C. The structure was refined to the final error indices *R*₁ = 0.073 and *R*₂ = 0.100 with 249 reflections for which *I* > 3σ(*I*). In this structure, Cd species (formally Cd²⁺, Cd⁺, and Cd⁰) are found at seven crystallographic sites. Twenty-eight Cd²⁺ ions per unit cell are found at three crystallographic sites: eight occupy site I' in the sodalite unit and associate with four Cd⁰ atoms near site II' to form four (Cd₃)⁴⁺ clusters [Cd²⁺–Cd⁰–Cd²⁺ = 105.2(7)°, Cd²⁺–Cd⁰ = 2.76(5) Å, Cd²⁺–O = 2.176(25) Å, Cd⁰–O = 3.03(5) Å] in four of the eight sodalite cavities per unit cell. The remaining 20 Cd²⁺ ions are found at sites II' and II with occupancies of six and 14 [trigonal, Cd–O = ca. 2.19(2) Å for both]. Thirty-six Cd⁺ ions are found at three crystallographic sites: six Cd⁺ ions are at site I, at the centers of the double six-oxygen rings [octahedral, Cd–O = 2.559(14) Å]; 18 Cd⁺ ions lie at site I', in the sodalite cavity opposite double six-oxygen rings [trigonal, Cd–O = 2.393(25) Å]; and 12 Cd⁺ ions occupy site II in the supercage [trigonal, Cd–O = 2.418–(23) Å]. Of the 46 Cd²⁺ cations initially present per unit cell, 18 have reacted to form 36 monatomic Cd⁺, and eight associate with four Cd⁰ atoms to give four (Cd₃)⁴⁺ cations. Highly reducing cadmium species are highly dispersed within the zeolite.

Introduction

Cations within zeolites are easily reduced by exposure to metal vapors. Cationic clusters, cationic continua, monatomic cations, and neutral metal clusters can form. Many examples involving alkali metal atoms and cations have been reported.^{1–3}

There are three previous reports of cadmium cluster formation within zeolites by metal vapor sorption. A (Cd₃)⁴⁺ cluster of low symmetry (Cd²⁺–Cd⁰–Cd²⁺) was found in the large cavity of a cadmium sorption complex of Cd²⁺-exchanged zeolite A by single-crystal X-ray diffraction methods.⁴ Three of the six Cd²⁺ ions per unit cell had been reduced to Cd⁺. In an earlier report, a cadmium sorption complex of partially dehydrated Cd²⁺-exchanged zeolite A was found to contain Cd⁺ and Cd₂²⁺.⁵ Also, it was reported that the crystal structure of a zinc sorption complex of Cd²⁺-exchanged zeolite X contained tetrahedral Cd₂²⁺₄(μ₃-Zn⁰Cd²⁺Zn⁰)₄ clusters.⁶ The existence of Cd₃²⁺ and Cd₄²⁺ species had been postulated on the basis of Raman measurements.⁷

UV irradiation of aqueous solutions of Cd²⁺ produces highly unstable, strongly reducing monatomic Cd⁺ ions.^{8,9} Since Cd⁺ is not stable in aqueous solution, most attempts to study the univalent state have involved the dissolution of cadmium metal in molten cadmium dihalides.⁷

Cd⁺, whether mono- or binuclear, should be a very strong reducing agent within a zeolite; it would be highly dispersed and readily available to guest molecules. Beyond that, intrazeolitic cadmium clusters may have unique chemical and physical properties.

In this work, dehydrated Cd₄₆–X was exposed to Cd metal vapor with the hope that reduced species, perhaps clusters, would form within zeolite X. These species, their placement, and their structures would be observed crystallographically.

Experimental Section

Large single crystals of sodium zeolite X, stoichiometry Na₉₂–Si₁₀₀Al₉₂O₃₈₄, were prepared in St. Petersburg, Russia.¹⁰ One of these crystals, a colorless octahedron about 0.2 mm in cross-section, was lodged in a fine Pyrex capillary.

To prepare stoichiometrically Cd²⁺-exchanged zeolite X, a 0.05 M solution of Cd(NO₃)₂ (99.999% purity, Aldrich Chemical Co.) was used. It was allowed to flow past the crystal at a velocity of approximately 15 mm/s for 5 d at 21(1) °C. After dehydration at 460 °C and 2 × 10^{–6} Torr for 2 days, cadmium metal was introduced by distillation from a sidearm break-seal ampule to the Pyrex-tube extension of the crystal-containing capillary. This Pyrex reaction vessel was then sealed off from the vacuum system under vacuum and placed within two

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TABLE 1: Positional, Thermal, and Occupancy Parameters^a for Dehydrated Cd₆₈-X

atom	Wyc pos	formal		x	y	z	U_{11} or U_{iso} ^b	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	occupancy ^c	
		charge	site										varied	fixed
Si,Al	192(i)			-520(3)	1253(4)	359(3)	50(12)							192
O(1)	96(h)			-1013(8)	1014(7)	0	172(77)							96
O(2)	96(g)			-18(8)	-18(8)	1457(9)	97(60)							96
O(3)	96(g)			-706(7)	-706(7)	238(10)	183(70)							96
O(4)	96(g)			1732(8)	1732(8)	3192(10)	137(70)							96
Cd(1)	16(c)	1+	I	0	0	0	176(58)	176(58)	176(58)	42(69)	42(69)	42(69)	5.9(3)	6
Cd(2)	32(e)	2+	I'	628(8)	628(8)	628(8)	584(87)	584(87)	584(87)	225(110)	225(110)	225(110)	8.1(4)	8
Cd(3)	32(e)	1+	I'	721(3)	721(3)	721(3)	370(33)	370(33)	370(33)	58(42)	58(42)	58(42)	18.3(5)	18
Cd(4)	32(e)	0		1533(53)	1533(53)	1661(30)	1202(327)						4.05(17)	4
Cd(5)	32(e)	2+	II'	2075(15)	2075(15)	2075(15)	823(194)						5.7(5)	6
Cd(6)	32(e)	2+	II	2249(4)	2249(4)	2249(4)	216(36)	216(36)	216(36)	95(45)	95(45)	95(45)	13.4(4)	14
Cd(7)	32(e)	1+	II	2415(4)	2415(4)	2415(4)	250(45)	250(45)	250(45)	80(45)	80(54)	80(54)	12.2(4)	12

^a $a = 24.953(6)$ Å, space group $Fd\bar{3}m$, origin at center of symmetry. 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 = $\exp[(-2\pi^2/a^2)(U_{11}h^2 + U_{22}k^2 + U_{33}l^2 + U_{12}hk + U_{13}hl + U_{23}kl)]$. $B_{iso} = 8\pi^2 U_{iso}$. ^c Occupancy factors are given as the number of atoms or ions per unit cell.

adjacent coaxial horizontal cylindrical ovens. The crystal in one oven was exposed to 0.005 Torr of cadmium metal vapor at 320 °C for 9 days. (The vapor pressure of cadmium at 250 °C, the temperature of the second oven, is 0.005 Torr.) Then the extension of the crystal-containing capillary was cooled to room temperature to allow the cadmium vapor to condense away from the crystal. After cooling to room temperature, the resulting deep blue crystal was sealed off from the reaction vessel by torch.

The reflection conditions (hkl , $h + k$, $k + l$, $l + h = 2n$; $0kl$, $k + l = 4n$) indicate that the space group is either $Fd\bar{3}$ or $Fd\bar{3}m$. $Fd\bar{3}$ was initially chosen because most crystals from this synthesis batch, regardless of subsequent chemical treatment, have been refined successfully with $Fd\bar{3}$.¹¹ However, $Fd\bar{3}$ was rejected and the space group $Fd\bar{3}m$ was chosen because only an insignificant difference (0.005 Å) was seen in least-squares refinement between the mean Al–O and Si–O distances, and the error indexes did not increase when the space group was changed to $Fd\bar{3}m$. The near erasure of the differences between Al–O and Si–O distances indicates that the Si/Al composition at the Si position is essentially the same as that for the entire crystal: the long-range Si, Al ordering has been lost. (The same is true at the Al position.) This can occur most easily if antodomains have formed.¹²

Diffraction data were collected with an automated Enraf-Nonius four-circle computer-controlled CAD-4 diffractometer equipped with a pulse-height analyzer and a graphite monochromator, using Mo radiation ($K\alpha_1$, $\lambda = 0.70930$ Å; $K\alpha_2$, $\lambda = 0.71359$ Å). The unit cell constant at 21(1) °C, determined by least-squares refinement of 25 intense reflections for which $14^\circ < 2\theta < 22^\circ$, is $a = 24.953(6)$ Å. All 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 813 unique reflections examined, only the 249 reflections for which $I > 3\sigma(I)$ were used in subsequent structure determination; 495 were used in the final cycles of refinement. An absorption correction ($\mu R = 0.26$, $\rho_{cal} = 1.948$ g/cm³) was made empirically with a ψ scan.¹³ The calculated transmission coefficients ranged from 0.985 to 0.995. This correction had little effect on the final error indexes. Other details are the same as previously reported.¹⁴

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)] of fully dehydrated, partially Cu²⁺-exchanged zeolite Y.¹⁵ Because the SiO₄ and AlO₄ tetrahedra are indistinguishable in the space group $Fd\bar{3}m$, only the average

species, (Si,Al), is considered in this work. Isotropic refinement converged to an unweighted R_1 index, $(\sum |F_o| - |F_c|)/\sum F_o$, of 0.49 and a weighted R_2 index, $(\sum w(F_o - |F_c|)^2/\sum wF_o^2)^{1/2}$, of 0.58.

The initial difference Fourier function revealed four large peaks at (0.0, 0.0, 0.0), (0.07, 0.07, 0.07), (0.241, 0.241, 0.241), and (0.209, 0.209, 0.209). Anisotropic refinement including these peaks as Cd(1), Cd(3), and Cd(7) and isotropic refinement of the fourth peak as Cd(5) converged with $R_1 = 0.16$ and $R_2 = 0.18$. Their occupancies refined to 5.8(3), 26.2(6), 12.3(4), and 5.7(5) ions/unit cell, respectively.

An ensuing difference Fourier function revealed two strong peaks at (0.153, 0.165, 0.165) and (0.224, 0.224, 0.224). Isotropic refinement of the first peak as Cd(4) and anisotropic refinement of the second peak as Cd(6) converged with $R_1 = 0.11$ and $R_2 = 0.14$. Their occupancies refined to 4.1(5) and 13.5(5), respectively. The thermal ellipsoids at Cd(3) became very elongated in subsequent refinements so it was split into two positions, Cd(2) and Cd(3). Occupancy refinement of the cadmium ions at Cd(2) converged at 8.1(4); this value was fixed at eight ions (see Table 1), two times the number of Cd⁰ atoms at Cd(4). The eight Cd²⁺ ions at Cd(2) associate with the four Cd⁰ atoms at Cd(4) (site II') to form four Cd²⁺–Cd⁰–Cd²⁺ clusters, (Cd₃)⁴⁺.

Simultaneous positional, occupancy, and isotropic refinement of all but Cd(1), Cd(2), Cd(3), Cd(6), and Cd(7), which were refined anisotropically, converged to $R_1 = 0.073$ and $R_2 = 0.100$. The goodness-of-fit is $[\sum w(F_o - |F_c|)^2/(m - s)]^{1/2} = 5.4$, where m (249) is the number of observations and s (35) is the number of variables in least-squares refinement. The final difference function was featureless. The final refinement was done with the 495 reflections for which $I > 0$ to make better use of the diffraction data: $R_1 = 0.14$ and $R_2 = 0.11$. In the final cycle of least-squares refinement, all shifts in atomic parameters were less than 0.1% of their corresponding standard deviations.

Atomic scattering factors^{16,17} for (Si,Al)^{1.75+} (the mean of Si⁰, Si⁴⁺, Al⁰, and Al³⁺), O⁻, and Cd²⁺ were used. All scattering factors were modified to account for anomalous dispersion.¹⁸ 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 vertexes known as the sodalite cavity or β cage may be viewed as the principal building block of the aluminosilicate framework of the zeolite

TABLE 2: Selected Interatomic Distances and Angles^a

(Si,Al)—O(1)	1.620(16)	O(1)—(Si,Al)—O(2)	111.9(8)
(Si,Al)—O(2)	1.661(15)	O(1)—(Si,Al)—O(3)	109.0(8)
(Si,Al)—O(3)	1.729(19)	O(1)—(Si,Al)—O(4)	113.4(10)
(Si,Al)—O(4)	1.663(16)	O(2)—(Si,Al)—O(3)	103.3(10)
		O(2)—(Si,Al)—O(4)	107.1(11)
		O(3)—(Si,Al)—O(4)	111.6(7)
Cd(1)—O(3)	2.559(14)		
Cd(2)—O(3)	2.176(25)		
Cd(3)—O(3)	2.393(25)	(Si,Al)—O(1)—(Si,Al)	145.6(9)
Cd(4)—O(2)	3.03(5)	(Si,Al)—O(2)—(Si,Al)	138.0(15)
Cd(5)—O(2)	2.196(26)	(Si,Al)—O(3)—(Si,Al)	126.7(15)
Cd(6)—O(2)	2.193(22)	(Si,Al)—O(4)—(Si,Al)	148.1(17)
Cd(7)—O(2)	2.418(23)		
		O(3)—Cd(1)—O(3)	81.1(7), 98.9(7)
Cd(1)—Cd(2)	2.712(11) ^b	O(3)—Cd(2)—O(3)	99.8(5)
Cd(2)—Cd(4)	2.76(5)	O(3)—Cd(3)—O(3)	88.1(5)
Cd(1)—Cd(3)	3.117(4)	O(2)—Cd(4)—O(2)	72.4(6)
Cd(3)—Cd(4)	2.44(3) ^b	O(2)—Cd(5)—O(2)	117.0(6)
Cd(4)—Cd(6)	2.74(9) ^b	O(2)—Cd(6)—O(2)	117.3(6)
		O(2)—Cd(7)—O(2)	101.5(5)
		Cd(2)—Cd(4)—Cd(2)	105.2(7)

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

^b Readily avoidable by cation placement within partially occupied equipoints. Distances are given in Ångströms; angles are given in degrees.

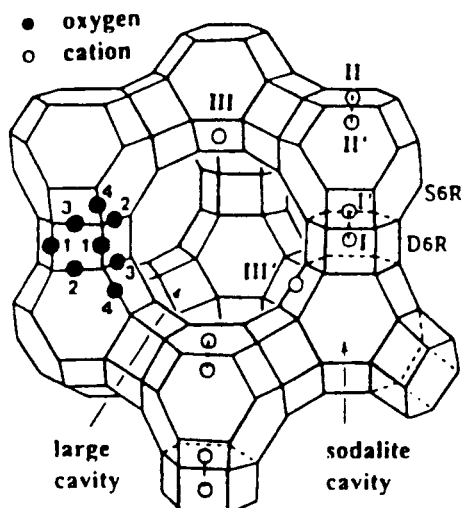


Figure 1. Stylized drawing of the framework structure of zeolite X. Near the center of each line segment is an oxygen atom. The different oxygen atoms are indicated by the numbers 1–4. Silicon and aluminum atoms alternate at the tetrahedral intersections, except that a silicon atom substitutes for aluminum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

(see Figure 1). These β -cages are connected tetrahedrally at six-rings by bridging oxygens to give double six-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 midway 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 that 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 cavity on the opposite side of either of the D6R's six-rings from site I, II' inside the sodalite cavity near a single six-ring (S6R) entrance to the supercage, II in the supercage adjacent to a S6R, III in the supercage on a 2-fold axis opposite a four-ring between

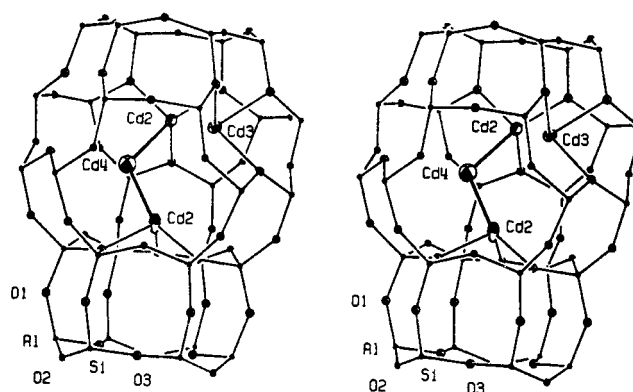


Figure 2. Stereoview of about 50% of the sodalite cavities in $\text{Cd}_{68}\text{-X}$. A $\text{Cd}^{2+}\text{-Cd}^0\text{-Cd}^{2+}$ cluster [two Cd^{2+} ions at Cd(2) (site I') and one Cd^0 atom at Cd(4) (site II')] is shown. One Cd^+ ion at Cd(3) (site I') is also shown. Ellipsoids of 20% probability are used.

two 12-rings, and III' off the 2-fold axis, somewhat or substantially distant from III but otherwise near the inner walls of the supercage.^{19,20}

The mean value of the (Si,Al)—O bond length is 1.67 Å, nicely the average of mean Si—O (1.61 Å) and Al—O (1.72 Å) distances.¹¹ The individual bond lengths, however, show marked variations ranging from 1.62(2) to 1.73(2) Å. These (Si,Al)—O distances depend on cadmium ion coordination to framework oxygen, and cadmium ions coordinate only to O(2) and O(3). As a consequence of these interactions, the (Si,Al)—O(2) and (Si,Al)—O(3) bonds are generally longer than (Si,Al)—O(1) and (Si,Al)—O(4). This effect is frequently observed, for example in dehydrated $\text{Cd}_{46}\text{-X}$,²¹ and is seen (less definitively) here (see Table 2).

In this crystal structure, Cd ions and atoms occupy seven crystallographic sites, indicating a structure of unexpected complexity. The distances between Cd species, $\text{Cd}(i)$, $i = 1\text{--}7$, and their closest framework oxygens range widely; they are 2.559(14), 2.176(25), 2.393(25), 3.03(5), 2.196(26), 2.193(22), and 2.418(23) Å, respectively. For comparison, the sum of the conventional ionic radii of Cd^{2+} and O^{2-} is $0.97 + 1.32 = 2.29$ Å,²² and that of Cd^+ and O^{2-} is $1.14 + 1.32 = 2.46$ Å.^{22,23} Considering these widely ranging yet nicely clustering distances, formal charges (Cd^{2+} , Cd^+ , and Cd^0) may be assigned as follows: the species at Cd(2), Cd(5), and Cd(6) may be identified as Cd^{2+} ions [$\text{Cd}\text{-O} = 2.176(25)$, $2.196(26)$, and $2.193(22)$ Å, respectively]; those at Cd(1), Cd(3), and Cd(7) as Cd^+ ions [$\text{Cd}\text{-O} = 2.559(14)$, $2.393(25)$, and $2.418(23)$ Å; coordination numbers = 6, 3, and 3, respectively]; and those at Cd(4) as Cd atoms [$\text{Cd}\text{-O} = 3.03(5)$ Å, see Table 1]. This assignment gives a total positive charge that nicely balances the anionic charge of the zeolite framework.

Twenty-eight Cd^{2+} ions per unit cell are found at three crystallographic sites I', II', and II. (1) Eight Cd^{2+} ions at Cd(2) occupy site I', on a 3-fold axis in the sodalite unit opposite D6Rs (see Figure 2). (This is a 32-fold position, but it is occupied by only eight Cd^{2+} ions and 18 Cd^+ ions.) Each Cd^{2+} ion lies relatively far inside the sodalite cavity, 1.45(8) Å from the plane of the three O(3) framework oxygens of the D6R to which it is bound. The $\text{Cd}(2)\text{-O}(3)$ distances are 2.176(25) Å, somewhat shorter than the sum of corresponding ionic radii, $0.97 + 1.32 = 2.29$ Å,²² indicating that each Cd^{2+} ion coordinates strongly to its three O(3) oxygens as would be expected by its low coordination number. (2) Six Cd^{2+} ions at Cd(5) occupy site II', on 3-fold axes inside the sodalite cavity near a single six-ring entrance to the supercage [trigonal, $\text{Cd}(5)\text{-O}(2) = 2.196(26)$ Å (again less than the sum of the

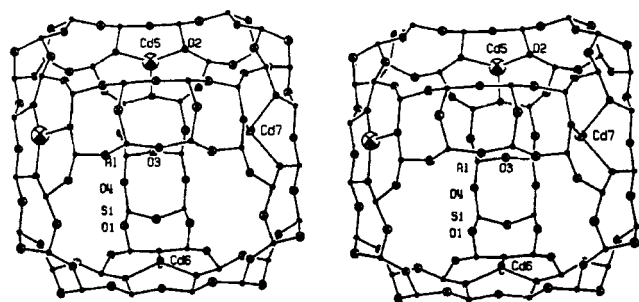


Figure 3. Stereoview of a supercage. Two Cd^{2+} ions at Cd(5) (site II'), one Cd^+ ion at Cd(6) (site II), and one Cd^+ ion at Cd(7) (site II) are shown. Ellipsoids of 20% probability are used.

TABLE 3: Deviations of Atoms and Ions from (111) Planes

position	cation site	displacement (\AA)
At O(2) ^{a,b}		
Cd(4)	(atom)	-2.361
Cd(5)	II'	-0.386
Cd(6)	II	0.365
Cd(7)	II	1.082
At O(3) ^{b,c}		
Cd(1)	I	-1.690
Cd(2)	I'	1.024
Cd(3)	I'	1.426

^a A positive displacement indicates that the ion lies in the supercage.
^b Sites I' and II' are in the sodalite units. ^c The negative displacement indicates that the ion lies within a double six-ring.

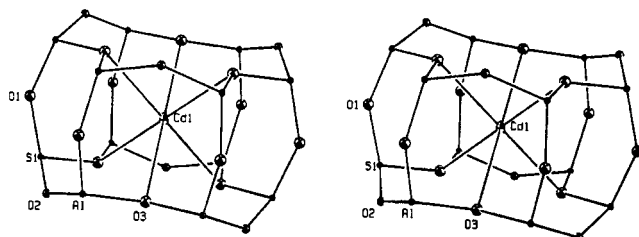


Figure 4. Stereoview of a double six-ring of $\text{Cd}_{68}\text{-X}$. Six of the 16 D6Rs per unit cell contain an octahedral Cd^+ ion at Cd(1), site I. Ellipsoids of 20% probability are used.

conventional ionic radii), $\text{O}(2)\text{-Cd}(5)\text{-O}(2) = 117.0(6)^\circ$, see Figure 3]. (3) The remaining 14 Cd^{2+} ions at Cd(6) are at site II in the supercage (see Figure 3); each of these Cd^{2+} ions is 2.193(22) \AA from its nearest neighbors, three O(2) framework oxygens. These trigonal $\text{Cd}(6)\text{-O}(2)$ distances are a little shorter than the sum of the conventional ionic radii of $0.97 + 1.32 = 2.29 \text{ \AA}$,²² presumably because these cadmium ions, like Cd(2) and Cd(5), are only three-coordinate. Similarly shortened distances were seen previously in dehydrated $\text{Cd}_{46}\text{-X}$.²¹ These Cd^{2+} ions are recessed a little, 0.365 \AA , into the supercage from the plane of the three O(2) oxygens (see Table 3).

Thirty-six Cd^+ ions are found at three crystallographic sites. (1) Six Cd^+ ions at Cd(1) occupy the octahedral site I, at the centers of the double six-oxygen rings (see Figure 4). This octahedral $\text{Cd}(1)\text{-O}(3)$ distance, 2.559(14) \AA , is a little longer than the sum of the ionic radii of Cd^+ and O^{2-} , $1.14 + 1.32 = 2.46 \text{ \AA}$, indicating a reasonably good fit. (2) Eighteen Cd^+ ions at Cd(3) occupy site I', in the sodalite cavity opposite double six-oxygen rings [trigonal, $\text{Cd}(3)\text{-O}(3) = 2.393(25) \text{ \AA}$, $\text{O}(3)\text{-Cd}(3)\text{-O}(3) = 88.1(5)^\circ$, see Figure 5]. (3) Twelve Cd^+ ions at Cd(7) occupy site II in the supercage [trigonal, $\text{Cd}(7)\text{-O}(2) = 2.418(23) \text{ \AA}$, $\text{O}(2)\text{-Cd}(7)\text{-O}(2) = 101.5(5)^\circ$, see Figure 3]. The latter two $\text{Cd}\text{-O}$ distances are just a little shorter than the

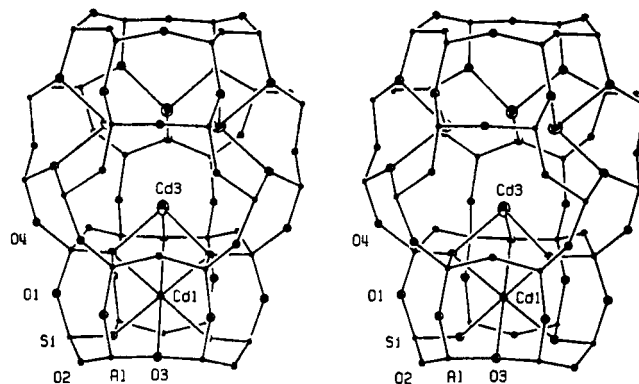


Figure 5. Stereoview of about 25% of the sodalite cavities in $\text{Cd}_{68}\text{-X}$. Four Cd^+ ions [Cd(3)] are shown at site I'. The remaining 25% of the sodalite cavities have only three Cd^+ ions at Cd(3). Ellipsoids of 20% probability are used.

sum of the corresponding ionic radii of Cd^+ and O^{2-} , $1.14 + 1.32 = 2.46 \text{ \AA}$, because of their low coordination number.

Four Cd^0 atoms are at Cd(4), nearly at site II', in the sodalite unit. Each associates with two Cd^{2+} ions, Cd(2), at site I' to form a bent $(\text{Cd}_3)^{4+}$ cluster [$\text{Cd}^{2+}\text{-Cd}^0 = 2.76(5) \text{ \AA}$, $\text{Cd}^{2+}\text{-Cd}^0\text{-Cd}^{2+} = 105.2(7)^\circ$, see Figure 2] in four of the eight sodalite cavities per unit cell. The $\text{Cd}(4)\text{-Cd}(2)$ distance, 2.76(5) \AA , is not too different from the sum (2.46 \AA) of the atomic radius of Cd (1.49 \AA) and the ionic radius of Cd^{2+} (0.97 \AA) and is therefore reasonable. This cadmium cluster is stabilized by charge delocalization within itself and by interaction with 6-ring oxygens.

Finally, long but significant 3.117(4) \AA $\text{Cd}^+\cdots\text{Cd}^+$ contacts are seen between the Cd(1) and Cd(3) positions. These are much longer than the ca. 2.35 \AA bonds seen in Cd_2^{2+} .⁴ They must occur because the occupancy rule, (number at site I) + (number at site I')/2 = 16, required for all short contacts about the D6Rs to be avoided, is violated. In this structure the sum is (see Table 1) $6 + 8/2 + 18/2 = 19$. To minimize repulsive forces, it is more reasonable that the close contacts which must occur are $\text{Cd}^+\cdots\text{Cd}^+$ rather than $\text{Cd}^+\cdots\text{Cd}^{2+}$. To avoid odd-electron species, it is more reasonable that $\text{Cd}^+\cdots\text{Cd}^+$ exists rather than $\text{Cd}^+\cdots\text{Cd}^{2+}$ or $\text{Cd}^+\cdots\text{Cd}^+\cdots\text{Cd}^+$. If each of the six ions at Cd(1) interacts at 3.117(4) \AA with a Cd^+ ion at Cd(3), all other intercationic distances would be acceptably long. Ignoring the six of the 18 Cd^+ ions at Cd(3), which would bond weakly to the Cd^+ ions at Cd(1), the sum becomes $6 + 8/2 + 12/2 = 16$. A similar rule for sites II and II', (number at site II) + (number at site II') = 32, is obeyed: $6 + 14 + 12 = 32$ (see Table 1). Accordingly, all S6Rs and D6Rs are full with Cd^+ , Cd^{2+} , and $\text{Cd}^+\cdots\text{Cd}^+$.

In summary, dehydrated $\text{Cd}_{46}\text{Si}_{100}\text{Al}_{92}\text{O}_{384}$ sorbed 22 cadmium atoms/unit cell to give $\text{Cd}_{68}\text{Si}_{100}\text{Al}_{92}\text{O}_{384}$ when exposed to 0.005 Torr of Cd(g) at 320 $^\circ\text{C}$. Eighteen of those sorbed cadmium atoms have reacted with 18 of the 46 Cd^{2+} ions to give 36 Cd^+ cations/unit cell. The remaining four sorbed cadmium atoms associate with eight of the remaining 28 Cd^{2+} ions to give four bent $(\text{Cd}_3)^{4+}$ cations in four of the eight sodalite cavities per unit cell.

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Supporting Information Available: Table of calculated and observed structure factors. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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