

# Zero-Coordinate Cadmium(II). Over Ion Exchange. Crystal Structures of Hydrated and Dehydrated Zeolite A Exchanged with CdCl<sub>2</sub> to Give Cd<sub>9.5</sub>Cl<sub>4</sub>(OH)<sub>3</sub>-A

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**Abstract:** The crystal structures of vacuum-dehydrated ( $a = 12.269$  (1) Å) and hydrated ( $a = 12.219$  (2) Å) zeolite A exhaustively exchanged with aqueous CdCl<sub>2</sub> at 25 °C have been determined by single-crystal x-ray diffraction techniques in the cubic space group  $Pm\bar{3}m$ . The structures were refined to final  $R$  (weighted) indexes of 0.039 and 0.061, respectively. In either structure, 9.5 Cd<sup>2+</sup> ions (a 58% overexchange), 4 Cl<sup>-</sup> ions, and 3 OH<sup>-</sup> ions (the hydrogens were not located) are found per unit cell. In the dehydrated structure, three Cd<sup>2+</sup> ions are on threefold axes in the sodalite unit where each coordinates to three oxide ions of the zeolite framework and to one OH<sup>-</sup> ion in a near-tetrahedral manner. Four Cd<sup>2+</sup> ions are located at other threefold-axis positions in the large cavity where each coordinates to three oxide ions of the zeolite framework and to one Cl<sup>-</sup> ion. Two more Cd<sup>2+</sup> ions bridge between pairs of these four Cl<sup>-</sup> ions and also approach one framework oxide ion at 2.6 Å. The remaining one-half Cd<sup>2+</sup> ion per unit cell is at the very center of an 8-oxygen ring at a site of  $D_{4h}$  symmetry. It is 3.55 Å from the four nearest framework oxide ions and 3.68 Å from four other oxide ions, all members of a planar 8-ring. This Cd<sup>2+</sup> ion is approximately 1.26 Å further from its nearest neighbors than the sum of the ionic radii, and can accordingly, by a distance criterion, be considered zero coordinate. In the hydrated structure, seven Cd<sup>2+</sup> ions are distributed over four threefold-axis positions: three are located almost in the 6-ring planes where each coordinates to three 6-ring oxide ions and, in the sodalite unit, to one OH<sup>-</sup> ion; one Cd<sup>2+</sup> ion is in the sodalite unit coordinated to three 6-ring oxide ions (and possibly an unlocated H<sub>2</sub>O molecule); two Cd<sup>2+</sup> ions are in the large cavity coordinated to three 6-ring oxide ions and one Cl<sup>-</sup> ion; and one is deep in the large cavity where it is tetrahedrally coordinated to four H<sub>2</sub>O molecules, three of which are within hydrogen bonding distance of framework oxide ions. Another Cd<sup>2+</sup> ion is located in the center of an 8-ring where it lies on a line between two coordinating Cl<sup>-</sup> ions. The remaining 1.5 Cd<sup>2+</sup> ions at a general position are each coordinated to a Cl<sup>-</sup> ion and possibly to unlocated H<sub>2</sub>O molecules. It is clear that ions such as CdCl<sup>+</sup> and CdOH<sup>+</sup> have participated extensively in the ion exchange process.

## Introduction

A zero-coordinate<sup>1,2</sup> Eu(II) ion is found in the structure of Eu(II)-exchanged zeolite A which had been exposed to Cl<sub>2</sub> at 25 °C.<sup>3</sup> That is, the distances between that Eu(II) ion and its nearest neighbors, four oxide ions of the zeolite framework, exceed the sum of the ionic radii by 1.19 Å. A Eu(II) ion is 0.96 Å too far from its nearest neighbors in dehydrated Eu<sub>5.5+x</sub>-Na<sub>1-2x</sub>-A,<sup>4</sup>  $0 \leq x \leq 0.5$ ;<sup>5</sup> because this distance discrepancy is unusually large, but less than 1 Å, this Eu(II) ion is referred to as near zero coordinate. One near zero coordinate dipositive ion per unit cell is found in fully dehydrated Ca<sub>6</sub>-A<sup>6,7</sup> (distance discrepancy = 0.77 Å) and in fully dehydrated Sr<sub>6</sub>-A<sup>6</sup> (distance discrepancy = 0.52 Å). These are the only fully dipositive-ion-exchanged zeolite A samples to be studied crystallographically in their dehydrated forms. Several examples of zero-coordinate monopositive ions, K<sup>+</sup> and Rb<sup>+</sup>, have been reported.<sup>1,2,8,9</sup>

This work was initiated to learn the arrangement of Cd<sup>2+</sup> ions within the dehydrated form of Cd<sup>2+</sup>-exchanged zeolite A. Upon dehydration, the somewhat rigid zeolite framework could require the Cd<sup>2+</sup> ions to adopt unusual coordination geometries with low coordination numbers, perhaps including zero. It was hoped that the greater covalent character of Cd<sup>2+</sup>, as compared to Ca<sup>2+</sup>, Sr<sup>2+</sup>, and Eu<sup>2+</sup>, would lead to a structural result which would serve to extend current views of zero coordination. It was reported that fully Cd<sup>2+</sup>-exchanged zeolite A, Cd<sub>6</sub>-A, is easily prepared using aqueous CdCl<sub>2</sub>.<sup>10</sup> Because Cd<sup>2+</sup> ions are relatively strong x-ray scatterers, locating them was expected to be unambiguous and precise.

The structure of the hydrated crystal was determined to verify the unexpected cation and anion composition of the dehydrated material, Cd<sub>9.5</sub>Cl<sub>4</sub>(OH)<sub>3</sub>-A, and to learn the structural basis for this unusual ion-exchange end point. This is the most extreme example of overexchange encountered in zeolite A to date; a single extra molecule of TlOH was observed per unit cell in hydrated Tl<sub>13</sub>(OH)-A.<sup>11</sup>

## Experimental Section

Crystals of zeolite 4A were prepared by a modification of Charnell's method,<sup>12</sup> including a second crystallization using seed crystals from the first synthesis. A single crystal 0.08 mm on an edge was lodged in a fine glass capillary. The exchange was then performed using flow methods; 0.05 M aqueous CdCl<sub>2</sub> was allowed to flow past the crystal at a velocity of approximately 5 mm/s. This procedure was conducted at 25 (1) °C for 48 h. The crystal was then dehydrated for a period of 48 h at 500 °C and  $5 \times 10^{-6}$  Torr. After cooling to room temperature, the crystal, still under vacuum, was sealed in its capillary by torch. Microscopic examination showed that the crystal was clear and colorless. The hydrated crystal (0.09 mm on an edge) used in this study was prepared by the same exchange procedure (flow velocity approximately 11 mm/s), and appeared white. Subsequent diffraction intensities were collected at 27 (1) °C for the dehydrated crystal and at 25 (1) °C for the hydrated one.

It was not clear to us at the time of our crystal preparation that exchange using CdCl<sub>2</sub> solution had been followed by extensive washing with warm, high-purity distilled water in previous work.<sup>10,13</sup> Consequently, the ion-exchange procedure used in all of our zeolite A single crystal preparations, which does not include a washing step, was followed.

The cubic space group  $Pm\bar{3}m$  (no systematic absences) appeared to be appropriate.<sup>4a,14-16</sup> A Syntex four-circle computer-controlled diffractometer with a graphite monochromator and a pulse-height analyzer was used throughout for preliminary experiments and for the collection of diffraction intensities. Molybdenum radiation ( $K\alpha_1$ ,  $\lambda = 0.709$  30 Å;  $K\alpha_2$ ,  $\lambda = 0.713$  59 Å) was used throughout. In each case, the cell constant,  $a = 12.269$  (1) Å for the dehydrated crystal and 12.219 (2) Å for the hydrated crystal, was determined by a least-squares treatment of 15 intense reflections for which  $20^\circ < 2\theta < 24^\circ$ .

For each crystal, reflections from two intensity-equivalent regions of reciprocal space ( $hkl$ ,  $h \leq k \leq l$ , and  $\bar{h}\bar{k}l$ ,  $k \leq h \leq l$ , for the dehydrated crystal, and  $hkl$ ,  $h \leq k \leq l$ , and  $\bar{h}\bar{k}l$ ,  $h \leq k \leq l$ , for the hydrated crystal) were examined using the  $\theta$ - $2\theta$  scan technique. Each reflection was scanned at a constant rate of 1.0 deg min<sup>-1</sup> from 1° (in  $2\theta$ ) below the calculated  $K\alpha_1$  peak to 1° above the  $K\alpha_2$  maximum. Background intensity was counted at each end of a scan range for a time equal to half the scan time. The intensities of three reflections

Table I. Positional, Thermal,<sup>a</sup> and Occupancy Parameters for Cd<sub>9.5</sub>Cl<sub>4</sub>(OH)<sub>3</sub>-A

	Wyckoff position	x	y	z	$\beta_{11}^b$ or $B_{iso}^c$					occupancy factor <sup>d</sup>		
					$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	fixed	varied	
a. Dehydrated												
(Si,Al)	24(k)	0	1825 (2)	3680 (2)	20 (2)	17 (2)	14 (2)	0	0	2 (3)	24 <sup>e</sup>	24 <sup>e</sup>
O(1)	12(h)	0	2000 (8)	1/2	65 (9)	36 (9)	19 (7)	0	0	0	12	12
O(2)	12(i)	0	2954 (5)	2954 (5)	41 (8)	24 (5)	24 (5)	0	0	27 (13)	12	12
O(3)	24(m)	1128 (3)	1128 (3)	3285 (5)	29 (3)	29 (3)	47 (6)	13 (9)	10 (7)	10 (7)	24	24
Cd(1)	8(g)	1568 (3)	1568 (3)	1568 (3)	53 (2)	53 (2)	53 (2)	56 (4)	56 (4)	56 (4)	3.0	2.68 (3)
Cd(2)	8(g)	2174 (1)	2174 (1)	2174 (1)	29 (1)	29 (1)	29 (1)	11 (3)	11 (3)	11 (3)	4.0	4.18 (4)
Cd(3)	24(l)	1516 (15)	3501 (11)	1/2	181 (20)	59 (11)	101 (13)	-154 (24)	0	0	2.0	1.81 (6)
Cd(4)	3(c)	0	1/2	1/2	560 (112)	290 (44)	290 (44)	0	0	0	0.5	0.50 (4)
Cl	24(m)	2892 (18)	3469 (13)	3469 (13)	108 (23)	118 (16)	118 (16)	-4 (32)	-4 (32)	-18 (35)	4.0	3.7 (1)
OH(1)	24(m)	423 (61)	423 (61)	763 (96)	10 (4)						3.0	2.8 (2)
b. Hydrated												
(Si,Al)	24(k)	0	1814 (15)	3699 (4)	40 (5)	15 (5)	13 (5)	0	0	-3 (8)	24 <sup>e</sup>	24 <sup>e</sup>
O(1)	12(h)	0	2134 (14)	1/2	84 (21)	28 (17)	-8 (12)	0	0	0	12	12
O(2)	12(i)	0	2957 (11)	2957 (11)	77 (22)	12 (11)	12 (11)	0	0	29 (26)	12	12
O(3)	24(m)	1128 (8)	1128 (8)	3346 (11)	41 (8)	41 (8)	88 (17)	50 (23)	-25 (18)	-25 (18)	24	24
Cd(1)	8(g)	1971 (6)	1971 (6)	1971 (6)	68 (5)	68 (5)	68 (5)	24 (12)	24 (12)	24 (12)	3.0	2.93 (6)
Cd(2)	8(g)	2488 (9)	2488 (9)	2488 (9)	56 (5)	56 (5)	56 (5)	47 (15)	47 (15)	47 (15)	2.0	1.95 (4)
Cd(3)	8(g)	1292 (23)	1292 (23)	1292 (23)	6.1 (9)						1.0	0.94 (6)
Cd(4)	48(n)	2086 (77)	3777 (74)	4485 (78)	16 (4)						1.5	1.5 (2)
Cd(5)	3(c)	0	1/2	1/2	41 (4)						1.0	1.02 (5)
Cd(6)	8(g)	3300 (37)	3300 (37)	3300 (37)	19 (3)						1.0	1.01 (8)
OH(1)	8(g)	867 (47)	867 (47)	867 (47)	10 (4)						3.0	3.3 (3)
O(6A)	24(m)	2601 (110)	2601 (110)	4513 (159)	13 (8)						3.0	3.2 (5)
O(6B)	8(g)	4292 (93)	4292 (93)	4292 (93)	4 (7)						1.0	1.2 (2)
Cl(2)	24(m)	2208 (90)	3826 (68)	3826 (68)	6 (3)						2.0	2.1 (3)
Cl(5)	6(f)	2068 (85)	1/2	1/2	20 (4)						2.0	2.1 (4)

<sup>a</sup> Positional and anisotropic 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. See Figures 1 and 3 for the identities of the atoms. The anisotropic temperature factor =  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$ . <sup>b</sup> Root mean square displacements can be calculated from  $\beta_{ii}$  values using the formula  $\mu_i = 0.225a(\beta_{ii})^{1/2}$ . <sup>c</sup> Isotropic thermal parameter in units of  $\text{\AA}$ . <sup>d</sup> Occupancy factors are given as the number of atoms or ions per unit cell. <sup>e</sup> Occupancy for (Si) = 12; occupancy for (Al) = 12.

in diverse regions of reciprocal space were reported after every 100 reflections to monitor crystal and instrument stability. Only small, random fluctuations of these check reflections were noted during the course of data collection. All unique reciprocal lattice points (881 and 874 for the dehydrated and hydrated crystals, respectively) for which  $2\theta < 70^\circ$  were examined. The high upper limit for  $2\theta$  was chosen to give a more complete data set, even though few reflections with large  $2\theta$  values showed significant intensity.

The raw data for each region were corrected for Lorentz and polarization effects, including that due to incident beam monochromatization; the reduced intensities were merged; and the resultant estimated standard deviations were assigned to each averaged reflection by the computer program COMPARE.<sup>17</sup> Other details regarding data reduction have been discussed previously.<sup>11</sup> An absorption correction was expected to be unimportant and was not applied.<sup>18</sup>

Only those reflections in each merged data set for which the net count exceeded three times its corresponding esd were used in structure solution and refinement. This amounted to 278 unique reflections for the dehydrated crystal and 189 for the hydrated crystal.

In an attempt to get a larger data set for the hydrated crystal, another crystal was ion exchanged, and its diffraction intensities were gathered, but for this crystal only 136 reflections were observed to have  $I > 3\sigma(I)$ .

**Structure Determination. Dehydrated Crystal.** Full-matrix least-squares refinement was initiated using the atomic parameters of Cd(Ac)<sub>2</sub>-exchanged zeolite A,<sup>19</sup> which had been dehydrated at 400 °C, for the atoms of the aluminosilicate framework [(Si,Al), O(1), O(2), and O(3)] and for six Cd<sup>2+</sup> ions at threefold-axis positions in the sodalite unit. Anisotropic refinement of the Cd<sup>2+</sup> ion position resulted in a very elongated thermal ellipsoid, suggesting that there were two Cd<sup>2+</sup> ion positions rather than one. Isotropic, followed by anisotropic, refinement of two Cd<sup>2+</sup> ion positions converged to an  $R_1$  index,  $(\sum |F_o - |F_c||) / \sum F_o$ , of 0.147 and a weighted  $R_2$  index,  $(\sum w(F_o - |F_c|)^2 / \sum wF_o^2)^{1/2}$ , of 0.178. A subsequent difference Fourier function revealed three significant peaks. One, within coordinating

distance of Cd(2), was included in least-squares refinement as Cl<sup>-</sup>; a second peak, within coordinating distance of this Cl<sup>-</sup>, was included as Cd<sup>2+</sup>; the third peak, appearing at (0, 1/2, 1/2), a cation position found in several other zeolite A structures,<sup>1,5,6,8,11</sup> was also included as Cd<sup>2+</sup>. Least-squares refinement including these three positions, with occupancy and isotropic thermal parameters varying, converged with  $R_1 = 0.065$  and  $R_2 = 0.070$ . Further examination of the difference Fourier function indicated the presence of another atomic position in the sodalite unit. Least-squares refinement of this position as O<sup>-</sup> lowered the error indexes to  $R_1 = 0.058$  and  $R_2 = 0.047$ .

Simultaneous occupancy, positional, and thermal parameter refinement of all nonframework positions converged to the occupancies shown in the last column of Table Ia. These occupancies were revised, by the assumption of stoichiometry and the requirement that the structure be plausible, to the values given for the nonframework positions in the fixed occupancy factor column of Table Ia.

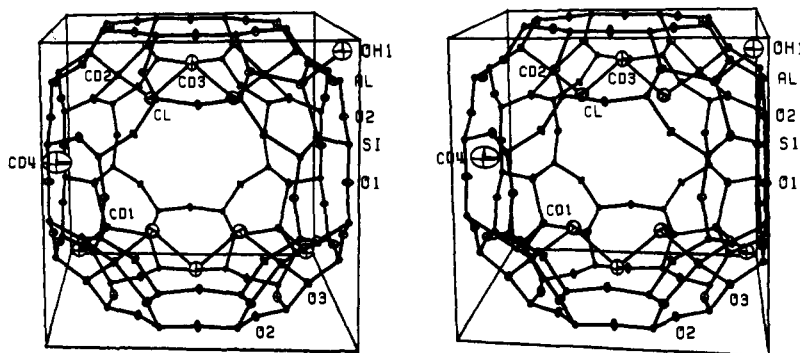
Since the OH(1) peak on the previous difference Fourier function was not well defined, another difference Fourier including all atomic positions except OH(1) was generated. Once again a diffuse region of electron density was apparent in the sodalite unit. Least-squares refinement of OH(1) at various symmetry positions (0,z,z; x,z,z; x,x,x; and x,x,z) resulted in comparable error indexes. However, omission of the OH(1) position increased  $R_1$  by 0.012 and  $R_2$  by 0.027. Anisotropic refinement of all positions except OH(1) which was refined isotropically (at (x,x,z) in order to maximize the OH(1)-OH(1) distances) converged with the final error indexes,  $R_1 = 0.056$  and  $R_2 = 0.039$ , at the fixed occupancies shown in Table Ia. The goodness of fit,  $(\sum w(F_o - |F_c|)^2 / (m - s))^{1/2}$ , is 1.89;  $m$  (278) is the number of observations, and  $s$  (44) is the number of variables in least squares. Ail shifts in the final cycle of refinement were less than 8% of their corresponding esd's.

The most significant peaks on the final difference Fourier function, whose estimated standard deviation is  $0.085 \text{ e } \text{\AA}^{-3}$  at a general position, were both  $0.6 \text{ e } \text{\AA}^{-3}$  in height and were located at (0.013, 0.141, 1/2) and (0.172, 0.172, 0.352), which are too close to O(1) and O(2), respectively, to be plausible atomic positions.

**Table II.** Selected Interatomic Distances (Å) and Angles (deg)<sup>a</sup>

a. Dehydrated			
(Si,Al)-O(1)	1.634 (3)	O(1)-(Si,Al)-O(2)	115.2 (5)
(Si,Al)-O(2)	1.647 (3)	O(1)-(Si,Al)-O(3)	110.4 (4)
(Si,Al)-O(3)	1.697 (2)	O(2)-(Si,Al)-O(3)	105.6 (4)
		O(3)-(Si,Al)-O(3)	109.2 (4)
Cd(1)-O(3)	2.241 (6)	(Si,Al)-O(1)-(Si,Al)	164.9 (5)
Cd(1)-O(2)	3.079 (7)	(Si,Al)-O(2)-(Si,Al)	155.4 (6)
Cd(1)-OH(1)	2.22 (6)	(Si,Al)-O(3)-(Si,Al)	137.7 (4)
Cd(2)-O(3)	2.270 (5)		
Cd(2)-O(2)	2.991 (4)	O(3)-Cd(1)-O(3)	113.3 (3)
Cd(2)-Cl	2.41 (2)	O(3)-Cd(1)-OH(1)	110 (2)
Cd(3)-Cl	2.53 (2)	O(3)-Cd(1)-OH(1)	97 (3)
Cd(3)-O(1)	2.62 (2)	O(3)-Cd(2)-O(3)	111.1 (3)
Cd(4)-O(2)	3.550 (9)	O(3)-Cd(2)-Cl	100.6 (6)
Cd(4)-O(1)	3.68 (1)	Cd(2)-Cl-Cd(3)	104.8 (8)
		Cl-Cd(3)-Cl	96 (1)
OH(1)-OH(1)	2.06 (7)		
b. Hydrated			
(Si,Al)-O(1)	1.64 (1)	O(1)-(Si,Al)-O(2)	109 (1)
(Si,Al)-O(2)	1.67 (1)	O(1)-(Si,Al)-O(3)	111.6 (8)
(Si,Al)-O(3)	1.667 (8)	O(2)-(Si,Al)-O(3)	106.3 (8)
		O(3)-(Si,Al)-O(3)	112 (1)
Cd(1)-O(3)	2.22 (1)	(Si,Al)-O(1)-(Si,Al)	152 (1)
Cd(1)-O(2)	2.95 (1)	(Si,Al)-O(2)-(Si,Al)	156 (1)
Cd(1)-OH(1)	2.3 (1)	(Si,Al)-O(3)-(Si,Al)	139 (1)
Cd(2)-O(3)	2.57 (2)		
Cd(2)-O(2)	3.149 (9)	O(3)-Cd(1)-O(3)	119 (1)
Cd(2)-Cl(2)	2.3 (1)	O(3)-Cd(1)-OH(1)	85 (2)
Cd(3)-O(3)	2.53 (2)	O(3)-Cd(2)-O(3)	96.3 (6)
Cd(3)-OH(1)	3.77 (9)	O(3)-Cd(2)-Cl(2)	94 (3)
Cd(4)-Cl(2)	2.1 (1)	O(3)-Cd(2)-Cl(2)	164 (3)
Cd(5)-Cl(5)	2.5 (1)	O(3)-Cd(3)-O(3)	98 (1)
Cd(5)-O(1)	3.51 (1)	O(6A)-Cd(6)-O(6A)	120 (12)
Cd(5)-O(2)	3.52 (2)	O(6A)-Cd(6)-O(6B)	94 (6)
Cd(6)-O(6A)	1.9 (2)	Cd(6)-O(6A)-O(3)	100 (8)
Cd(6)-O(6B)	2.1 (2)	Cd(2)-Cl(2)-Cd(4)	133 (6)
O(6A)-O(3)	2.9 (2)		
OH(1)-OH(1)	3.0 (1)		

<sup>a</sup> The numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding parameter.



**Figure 1.** A stereoview<sup>16</sup> of the large cavity of dehydrated CdCl<sub>2</sub>-exchanged zeolite A. Ellipsoids of 20% probability are shown.

The final structural parameters are presented in Table Ia. Interatomic distances and angles are given in Table IIa. A listing of observed and calculated structure factors is available; see paragraph at end of paper regarding supplementary material. Likely atomic arrangements in a particular unit cell and in a particular sodalite unit are shown in Figures 1 and 2, respectively.

**Hydrated Crystal.** Full-matrix least-squares refinement was initiated using the atomic parameters of the dehydrated structure for the framework atoms and for the two major Cd<sup>2+</sup> ion positions. The Cd(1) position was deleted because it did not refine well, and, the Cd(2) ion position refined with an elongated thermal ellipsoid, so it was split into two positions. These refined in least squares to occupancies of 3.1 and 2.2 Cd<sup>2+</sup> ions per unit cell (which were rounded to 3.0 and 2.0 and held fixed in subsequent refinements) and to the

error indexes  $R_1 = 0.196$  and  $R_2 = 0.191$ . A difference Fourier function revealed numerous peaks. The larger of these peaks with sensible distances from the framework or from the two Cd<sup>2+</sup> ion positions were included in successive least-squares refinements. This procedure resulted in the location of one ion at Cd(3), 1.5 at Cd(4), one at Cd(5), three at OH(1), and two at Cl(2);  $R_1 = 0.105$  and  $R_2 = 0.079$ .

A subsequent difference Fourier function revealed several well-defined positions. Four of the seven positions tried in least-squares refinement refined well as one ion at Cd(6), two at Cl(5), three atoms at O(6A), and one at O(6B). Because the data set was relatively small, only the Cd(1), Cd(2), and the framework positions were refined anisotropically.

Final refinement with occupancies fixed at the values indicated in

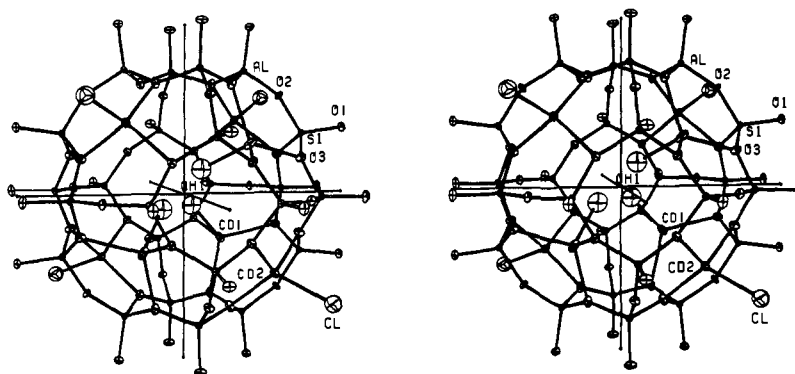


Figure 2. A stereoview<sup>16</sup> of the sodalite unit of dehydrated CdCl<sub>2</sub>-exchanged zeolite A. Ellipsoids of 20% probability are shown.

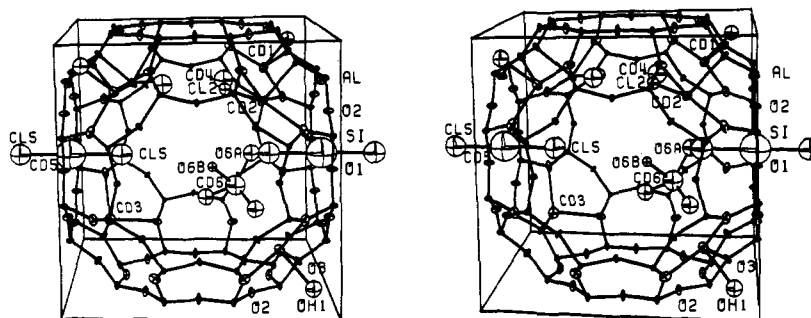


Figure 3. A stereoview<sup>16</sup> of the large cavity of hydrated CdCl<sub>2</sub>-exchanged zeolite A. Ellipsoids of 20% probability are shown. The  $\beta_{33}$  thermal parameter on O(1) was increased by  $2\sigma$  to give a positive-definite thermal ellipsoid.

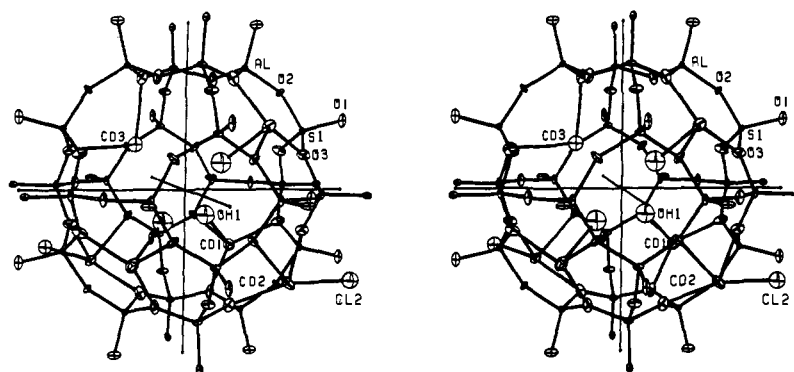


Figure 4. A stereoview<sup>16</sup> of the sodalite unit of hydrated CdCl<sub>2</sub>-exchanged zeolite A. Other comments in the caption to Figure 3 apply here as well.

Table Ib converged to the error indexes  $R_1 = 0.090$  and  $R_2 = 0.061$ . Simultaneous occupancy, positional, and thermal parameter refinement of all nonframework positions was ill behaved in least squares. The varied occupancies shown in the last column of Table Ib are the results of an occupancy-only refinement with all positional and thermal parameters fixed. The goodness of fit is 3.25; the number of observations is 189; and the number of parameters is 48 (including the 20 framework parameters). The overdetermination ratio,  $m/s$ , including all parameters is 3.9. However, if the 20 framework parameters, which are essentially stationary, are not included in the count of the number of variables, the ratio is 6.8. All shifts in the final cycle of refinement were less than 10% of their corresponding esd's, except for those of Cd(3) and OH(1) which were less than 21% of their corresponding esd's.

The most significant peak on the final difference Fourier function, whose estimated standard deviation is  $0.11 \text{ e } \text{\AA}^{-3}$ , was  $1.1 \text{ e } \text{\AA}^{-3}$  in height and was located at (0.062, 0.234, 0.375), too close (less than  $1.0 \text{ \AA}$ ) to the (Si,Al) position.

The final structural parameters are presented in Table Ib. Interatomic distances and angles are given in Table IIb. See paragraph at end of paper regarding supplementary material. Likely atomic ar-

rangements in a particular unit cell are shown in Figures 3 and 4.

The full-matrix least-squares program used<sup>17</sup> in all structure determinations minimized  $\sum w(\Delta|F|)^2$ ; the weight ( $w$ ) of an observation was the reciprocal square of  $\sigma$ , its standard deviation. Atomic scattering factors<sup>20,21</sup> for Cd<sup>2+</sup>, O<sup>-</sup>, Cl<sup>-</sup>, and (Si,Al)<sup>1.75+</sup> were used. The function describing (Si,Al)<sup>1.75+</sup> is the mean of the Si<sup>0</sup>, Si<sup>4+</sup>, Al<sup>0</sup>, and Al<sup>3+</sup> functions. The scattering factors for Cd<sup>2+</sup>, (Si,Al)<sup>1.75+</sup>, O<sup>-</sup>, and Cl<sup>-</sup> were modified to account for the real component ( $\Delta f'$ ) of the anomalous dispersion correction.<sup>22,23</sup>

## Discussion

**Dehydrated Crystal.** In the dehydrated crystal (Figure 1), three Cd<sup>2+</sup> ions at Cd(1) on the threefold axes are recessed  $0.59 \text{ \AA}$  into the sodalite unit from the O(3) planes of the 6-rings (Table III). Each of these Cd<sup>2+</sup> ions is coordinated to three O(3) framework oxide ions at  $2.241 (6) \text{ \AA}$  and to an OH(1) ion at  $2.22 (6) \text{ \AA}$  in a near-tetrahedral manner. The three OH(1) species hydrogen bond very strongly to each other at  $2.06 (7) \text{ \AA}$  (see Figure 2). (The symmetry of the OH(1) position was chosen to be  $(x,x,z)$  to allow the OH(1)-OH(1) distance to

**Table III.** Deviations of Atoms (Å) from the (111) Plane at O(3)<sup>a</sup>

dehydrated		hydrated	
Cd(1)	-0.59	Cd(1)	0.21
Cd(2)	0.69	Cd(2)	1.31
O(2)	0.26	Cd(3)	-1.23
OH(1)	-2.78	Cd(6)	3.02
Cl	3.04	O(2)	0.22
		Cl(2)	3.00
		O(6A)	2.89
		O(6B)	5.12
		OH(1)	-2.12

<sup>a</sup> A negative deviation indicates that the atom lies on the same side of the plane as the origin.

be maximized (vide supra)). Although the hydrogen atoms were not located, they must be present to allow the ions at OH(1) to be as close as they are. Also, to balance the charge of the excess number of Cd<sup>2+</sup> ions, they must be hydroxide ions and not water molecules.

Four Cd<sup>2+</sup> IONS AT Cd(2) are located on threefold axes and extend 0.69 Å into the large cavity from the [111] plane at O(3). Each of these Cd<sup>2+</sup> ions is coordinated to three O(3) oxide ions at 2.270 (5) Å and to one Cl<sup>-</sup> ion at 2.41 (2) Å. Each pair of these four chloride ions is, in turn, bridged by a coordinating Cd(3) ion at 2.53 (2) Å to complete a Cd(1)-Cl-Cd(3)-Cl-Cd(1) sequence between a pair of adjacent 6-rings. The ion at Cd(3) also approaches an O(1) oxide ion at 2.62 Å.

The remaining one-half Cd<sup>2+</sup> ion at Cd(4) is located at the center of an 8-ring, 3.55 Å from its four nearest neighbors at O(2), and 3.68 Å from its four next nearest neighbors at O(1). This Cd<sup>2+</sup> ion is approximately 1.26 Å further from O(2) than the sum of the ionic radii would indicate, therefore, on the basis of a distance criterion, is considered zero coordinate.<sup>2</sup>

Seven of the cations in the dehydrated structure may be considered monovalent (three CdOH<sup>+</sup> and four CdCl<sup>+</sup>), and 2.5 divalent. Two of these 2.5 are the bridging Cd(3) ions. The remaining one-half Cd<sup>2+</sup> ion could have occupied the remaining threefold-axis position near a 6-ring center, but instead is located at the center of an 8-ring. Similar situations have occurred previously in Ca<sup>2+</sup>, Sr<sup>2+</sup>, and Eu<sup>2+</sup> exchanged zeolite A structures.<sup>5,6</sup> Apparently, the presence of a Cd<sup>2+</sup> ion somewhere other than at the remaining 6-ring site results in a more even neutralization of the anionic charge of the zeolite framework, and in a minimization of intercationic repulsions.

The fact that a Cd<sup>2+</sup> ion is located at the center of an 8-ring rather than off to one side where it could approach some framework oxide ions at more conventional distances, indicates that a weaker interaction with four (or possibly eight) oxide ions is favored over stronger interactions with fewer oxide ions. Simple orbital considerations reveal that at this position of *D*<sub>4h</sub> symmetry (assuming that Si = Al and that the space group is *Pm*3*m*) both the 5s (*a*<sub>1g</sub>) and the 5p<sub>x</sub> and 5p<sub>y</sub> (*e*<sub>u</sub>) orbitals on Cd<sup>2+</sup> have the correct symmetry to accept electron density not only from the four oxide ions at O(2), but also from the four at O(1). The framework oxide ions at O(2) are closer to this Cd<sup>2+</sup> ion (3.55 Å) than are those at O(1) (3.68 Å) and therefore the Cd(4)-O(2) interactions may be presumed to be the more significant in the stabilization of Cd<sup>2+</sup> at this particular position.

**Hydrated Crystal.** The hydrated structure (Figure 3) was determined in order to confirm the unusual result obtained for the dehydrated crystal. Once again, 9.5 Cd<sup>2+</sup>, 4 Cl<sup>-</sup>, and 3 OH<sup>-</sup> ions per unit cell were located.

Three Cd<sup>2+</sup> ions at Cd(1) are on threefold axes, almost in the O(3) planes of three 6-rings (Table III). Each of these is coordinated at 2.3 (1) Å to an OH<sup>-</sup> ion in the sodalite unit and,

at 2.22 (1) Å, to three framework O(3) oxide ions. As in the dehydrated structure, these OH<sup>-</sup> ions are within hydrogen bonding distance of one another (see Table IIb and Figure 4), and must be OH<sup>-</sup> rather than H<sub>2</sub>O in order to preserve electrical neutrality.

Two more Cd<sup>2+</sup> ions are located at threefold-axis positions. One at Cd(6) lies deep within the large cavity where it coordinates tetrahedrally to four H<sub>2</sub>O molecules (the hydrogens were not located), three of which are within hydrogen bonding distance of framework O(3) oxide ions (see Figure 3 and Tables II and III). The second, at Cd(3), is recessed 1.23 Å into the sodalite unit (Figure 4) where it coordinates at 2.53 (2) Å to three O(3) oxide ions and possibly to an unlocated H<sub>2</sub>O molecule further into the sodalite unit. The somewhat long Cd(3)-O(3) distance may be attributed to the influence of the three OH<sup>-</sup> ions on the opposite side of the sodalite unit.

The Cd<sup>2+</sup> ion at Cd(5) is at the very center of an 8-ring, and is linearly coordinated at 2.51 Å to two Cl<sup>-</sup> ions at Cl(5) which extend perpendicularly above and below the 8-ring plane. The local symmetry at Cd(5) is *D*<sub>4h</sub> (in the space group *Pm*3*m*). Presumably, the Cl<sup>-</sup> ions interact with H<sub>2</sub>O molecules which are not at well-defined positions, because they could not be located.

Two Cd<sup>2+</sup> ions at Cd(2) on the threefold axes extend 1.31 Å into the large cavity from the [111] planes at O(3). In addition to the three O(3) oxide ions, each of these Cd<sup>2+</sup> ions is coordinated at 2.3 (1) Å to a Cl<sup>-</sup> ion at Cl(2) which is recessed further into the large cavity (Table III). Most of these Cl<sup>-</sup> ions, in turn, coordinate at 2.1 (1) Å to 1.5 Cd<sup>2+</sup> ions at Cd(4). The Cl(2) position, therefore, is an average of two positions—one where Cl<sup>-</sup> is coordinated to both Cd(2) and Cd(4), as must occur for 1.5 Cl<sup>-</sup> ions, and one where Cl<sup>-</sup> is coordinated to Cd(2) only (0.5 Cl<sup>-</sup> ions). The ions at the Cd(4) and Cl(2) positions can be arranged such that each ion at Cd(4) also makes a rather long approach (3.0 (1) Å) to a second Cl(2) ion (see Figure 3). This arrangement results in a somewhat more complete coordination situation for the ions at both Cd(4) and Cl(2), but also requires a 3.2 (1) Å Cd(4)-Cd(4) distance in those unit cells containing two Cd<sup>2+</sup> ions at Cd(4). Alternative distributions which avoid this short Cd(4)-Cd(4) approach are possible. The Cd<sup>2+</sup> ions at Cd(4) may coordinate to unlocated water molecules in addition to the Cl<sup>-</sup> ion at Cl(2). Cd(4) appears, by its fractional occupancy and inadequate coordination environment, to be the least satisfactory Cd<sup>2+</sup> site in the structure.

The short Cd-Cl bond lengths are consistent with the chemical situation. The gas-phase Cd-Cl bond length in CdCl<sub>2</sub> (in which Cd<sup>2+</sup> is two coordinate) was determined by electron diffraction to be 2.24 (3) Å,<sup>24</sup> which agrees well with the distances between Cd<sup>2+</sup> ions at Cd(2) and Cd(4) and Cl<sup>-</sup> ions at Cl(2). All these distances are considerably shorter than the 2.66 Å Cd-Cl bond length found in crystalline CdCl<sub>2</sub> (in which Cd<sup>2+</sup> is six coordinate).<sup>25</sup> The thermal ellipsoids at Cd(2) and Cl(2) are relatively small, indicating that these ions are firmly bound, whereas the ions at Cd(4) have more thermal motion and are less firmly positioned. These results are similar to those found in the chlorine sorption complex of partially dehydrated fully Ag<sup>+</sup>-exchanged zeolite A.<sup>26</sup>

Because the Cd(4) position had changed significantly during the course of several least-squares refinements from that originally found on a difference Fourier function, and because its complete coordination sphere could not be located, Cd(4) was removed from refinement. This caused the O(6A) position to become unstable and led to large increases in the error indexes to *R*<sub>1</sub> = 0.103 and *R*<sub>2</sub> = 0.087 from *R*<sub>1</sub> = 0.090 and *R*<sub>2</sub> = 0.061. The removal of O(6A) as well as Cd(4) led to convergence, but with the substantially higher error indexes *R*<sub>1</sub> = 0.109 and *R*<sub>2</sub> = 0.099. A difference Fourier function of this model with Cd(4) and O(6A) removed revealed diffuse regions

of electron density rather than distinct peaks at these two positions, indicating the presence of rather loosely held atoms.

**Over Ion Exchange.** An aqueous cadmium halide solution contains  $\text{Cd}^{2+}$ ,  $\text{CdX}^+$ ,  $\text{CdX}_2$ ,  $\text{CdX}_3^-$ ,  $\text{CdX}_4^{2-}$ , and  $\text{X}^-$  in equilibrium.<sup>27</sup> Since a  $\text{CdCl}_2$  solution is somewhat acidic, other species including  $\text{CdOH}^+$ ,  $\text{Cd}(\text{OH})_2$ , and  $\text{CdClOH}$  would also be expected to enter into this equilibrium. Consequently, the exchange solution used in this investigation contained both monovalent and divalent ions. The resulting structure with 9.5  $\text{Cd}^{2+}$  ions per unit cell may indicate a partial preference of the zeolite framework for monovalent ions, which can more evenly balance the local anionic charge of the zeolite framework. It is also apparent that  $\text{Cd}^{2+}$  prefers to complete its coordination sphere within the zeolite with anionic ligands ( $\text{OH}^-$  or  $\text{Cl}^-$  in this case) instead of  $\text{H}_2\text{O}$ .

Unpublished results<sup>19</sup> on the structures of zeolite A exchanged with 0.05 M cadmium acetate half-saturated with  $\text{Cd}(\text{OH})_2$  (pH ca. 7) indicate the exchange end point to be at  $\text{Cd}_{7.5}(\text{OH})_3\text{-A}$ , a 25% overexchange. Like the results reported herein, 3 equiv of hydroxide has exchanged into the zeolite per unit cell from relatively neutral solution, and is located within the sodalite unit.<sup>19</sup>

Over ion exchange into zeolite A appears to be unusual. It has been noted before only with  $\text{TlOH}$ , and there to a lesser extent (only 8%) than with  $\text{CdCl}_2$ . Over ion exchange was not observed with  $\text{KCl}$ ,<sup>9</sup>  $\text{KOH}$ ,<sup>9</sup>  $\text{RbOH}$ ,<sup>2</sup>  $\text{CsOH}$ ,<sup>8,28</sup>  $\text{CsNO}_3$ ,<sup>17</sup>  $\text{AgNO}_3$ ,<sup>29</sup>  $\text{Co}(\text{NO}_3)_2$ ,<sup>30</sup>  $\text{Mn}(\text{NO}_3)_2$ ,<sup>31</sup>  $\text{Zn}(\text{NO}_3)_2$ ,<sup>32</sup>  $\text{Ca}(\text{OH})_2$ ,<sup>6</sup>  $\text{Sr}(\text{OH})_2$ ,<sup>6</sup>  $\text{Ba}(\text{OH})_2$ ,<sup>33</sup> or  $\text{Eu}(\text{OH})_2$ .<sup>5</sup>

**Acknowledgments.** This work was supported by the National Science Foundation (Grant CHE-76 81585). We are indebted to the University of Hawaii Computing Center.

**Supplementary Material Available:** Listings of the observed and calculated structure factors for both structures (Supplementary Tables 1 and 2) (4 pages). Ordering information is given on any current masthead page.

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# Ring Opening of the *endo*-Alkoxytetraphenylcyclobutyl Ligand Coordinated to Palladium(II)

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**Abstract:** The reaction of  $\eta^3$ -*endo*-alkoxytetraphenylcyclobutenylpalladium chloride dimer with a variety of reagents leads to the formation of ring opened *cis*-1, *trans*-3-tetraphenyl-4-alkoxybutadien-1-yl complexes. Replacement of the chloride with either acac or hfac gave complexes which exist in solution as an equilibrium mixture of  $\eta^3$ -*endo*-alkoxytetraphenylcyclobutenyl  $\rightleftharpoons$   $\eta^3$ -butadienyl species ( $K_{eq} = 0.6-1.0$  in  $\text{CDCl}_3$ ). Reactions of these complexes with  $\text{Me}_2\text{PhP}$  gave  $\eta^1$ -butadienyl derivatives of the type  $[(\eta^1\text{-dienyl-C}_4\text{Ph}_4\text{OR})\text{PdX}(\text{Me}_2\text{PhP})_n]_n$  [ $\text{X} = \text{acac}$ ,  $n = 1$ ;  $\text{X} = \text{Cl}$ ,  $n = 2$  (solid),  $n = 1$  (solution)]. The  $\eta^3$ - and  $\eta^1$ -dienyl acac and hfac complexes exhibited temperature-dependent NMR spectra, which has been ascribed to a partial dissociation of a bidentate  $\beta$ -diketonate ligand to give a short-lived *three*-coordinate intermediate.

## Introduction

The cyclooligomerization reactions of acetylenes, catalyzed by palladium(II) chloride, are well known and recent investigations have shown these reactions to proceed via structurally unusual complex intermediates.<sup>1-3</sup> One of the first organo-

palladium compounds, derived from a reaction with an acetylene, to be structurally characterized is the complex *endo*-ethoxytetraphenylcyclobutenylpalladium(II) chloride dimer (**1**).<sup>4-9</sup> The formation of **1** must occur via a stereospecific reaction pathway since treatment of **1** with  $\text{HCl}$  to give  $[(\eta^4\text{-C}_4\text{Ph}_4)\text{PdCl}_2]_2$  followed by reaction with  $\text{NaOEt}$  gives the *exo*