Cadmium(I) and Dicadmium(I). Crystal Structures of Cadmium(II)-Exchanged Zeolite A Evacuated at 500 °C and of Its Cadmium Sorption Complex

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Abstract: The crystal structures of partially dehydrated, fully Cd^{2+}-exchanged zeolite A, $[Cd(H_2O)^{2+}]_3(Cd^{2+})_3$-A ($a$ = 12.242 (2) Å), and of its cadmium metal sorption complex, $[Cd(H_2O)^{2+}]_3(Cd^+)_3(Cd_2^{2+})_{1.5}$-A ($a$ = 12.291 (1) Å), have been determined by single-crystal X-ray diffraction techniques in the cubic space group $Pm3m$. The structures were refined to final R (weighted) indices of 0.039 and 0.062, respectively. All six Cd^{2+} ions in the unit cell of $[Cd(H_2O)^{2+}]_3(Cd^{2+})_3$-A are associated with 6-oxygen rings of the aluminosilicate framework. Three of these Cd^{2+} ions extend somewhat into the large cavity where each is three coordinate (Cd(II)-O ca. 2.17 Å) to three framework oxides. The other three Cd^{2+} ions are recessed into the sodalite unit where each is coordinated to three framework oxides and a fourth oxide (probably OH^- of a dissociated H_2O molecule) in a near-tetrahedral manner. Upon exposure to cadmium metal vapor the three three-coordinate Cd^{2+} ions react to form Cd^+ and Cd_2^{2+} species. The three four-coordinate ions move to the planes of 6-oxygen rings where each remains coordinated to three framework oxides and to one nonframework oxide; the latter, however, has moved to the large cavity. Three Cd^+ ions are found on threefold axes, each coordinated to three oxides of the zeolite framework (Cd(I)-O ca. 2.33 Å). Two of these are in the sodalite unit, and the other extends into the large cavity. One Cd_2^{2+} ion is located in the sodalite unit and is coordinated to the framework at one end only. The remaining $\frac{1}{2}Cd_2^{2+}$ ion per unit cell is symmetrically coordinated across an 8-oxygen ring in the large cavity. The Cd-Cd distance in Cd_2^{2+} is the same (2.35 Å) for the two modes of coordination. The existence of the univalent state of cadmium has been noted before in studies of cadmium metal dissolved in molten cadmium halides and in irradiated aqueous solutions of Cd^{2+}.

Introduction

Dehydration of Ag_{12}-A[1] results in the formation of silver atoms, probably as hexasilver molecules, in some of its sodalite units.[2] The extent to which such clusters form was found to depend on the dehydration conditions, and an apparent end point with a hexasilver occupancy of two-thirds was reached. To progress beyond this end point, it appeared that an additional source of silver atoms (other than Ag^+ ions reduced within the zeolite) would be needed. Silver metal itself, however, may not be a good source, for kinetic reasons, because of its negligible vapor pressure at allowable temperatures. An attempt to reduce some of the remaining Ag^+ ions within the zeolite using cadmium metal (vapor pressure 10^{-1} Torr at 321 °C[3]) as a reducing agent was unsuccessful—silver metal migrated out of the zeolite to form a Ag-Cd phase on the surface of the crystal.[4]

This work was initiated with the hope that, if dehydrated Cd_6-A were exposed to cadmium metal vapor, small cadmium metal clusters would form and be stabilized by the Cd^{2+} ions within the zeolite.

The formation of Cd_n^{m+} centers was considered another possible, and equally interesting, outcome of such an experiment. The existence of Cd_3^{2+} and Cd_4^{2+} species has been postulated on the basis of some Raman measurements.[5] Similar sodium species, with a single electron totally delocalized over several Na^+ ions, have been identified using ESR techniques in zeolite X (Na_6^{5+}),[6] zeolite Y (Na_4^{3+}),[7] and synthetic sodalite (Na_4^{3+})[8] which had been dehydrated and then exposed to sodium vapor. Analogous experiments with Na_{12}-A[4] and K_{12}-A[9] resulted in no reaction, presumably because all 6-ring sites are occupied and none are available for the additional ions which sorbed atoms would contribute to those structures. Since there are two such sites available in Cd_6-A, such a reaction could possibly occur.

The structure of Cd_6-A evacuated at 500 °C was determined because, although 500 °C appeared to be more than adequate to attain dehydration,[10] the Cd-exposed structure indicated the presence of three water molecules per unit cell.

Experimental Section

Crystals of zeolite 4A were prepared by Charnell's method.[11]

A single crystal, a cube 0.085 mm on an edge, was lodged in a fine quartz capillary. Ion exchange was performed using flow methods: 0.05 M aqueous $Cd(C_2H_3O_2)_2$ half-saturated with $Cd(OH)_2$ was allowed to flow past the crystal at a velocity of approximately 0.4 cm/s for 3 days at 25 °C. The crystal was washed by continuing this procedure using distilled water at 80 °C for 2 days. The washed crystal was dehydrated at 500 °C and 10^{-6} Torr for a period of 2 days, and, simultaneously, Cd metal was distilled from a side arm into the glass tubing above the capillary containing the crystal. This arrangement of distilled Cd and crystal was sealed, still under vacuum, from the main vacuum line. Finally, the crystal was exposed to Cd metal vapor by heating this vessel to 350 °C. The temperature was slowly decreased to 25 °C over a period of 2.5 days, and then the crystal, still under vacuum, was sealed in its capillary with a torch. Microscopic examination showed the crystal to be clear and colorless.

The second crystal (0.08 mm on an edge) used in this study was prepared by the same exchange (flow velocity approximately 0.7 cm/s for a period of 2 days), wash, and dehydration procedures. It also appeared clear and colorless. After the dehydration step, the crystal, still under vacuum, was cooled to 25 °C and sealed in its capillary with a torch.

Subsequent diffraction intensities for both crystals were collected at 25 (1) °C. The cubic space group $Pm3m$ (no systematic absences) appeared to be appropriate.[12] A Syntex four-circle computer-controlled diffractometer with a graphite monochromator and a pulse-height analyzer was used for preliminary experiments and for the collection of diffraction intensities. Molybdenum radiation ($K\alpha_1$, λ 0.709 30 Å; $K\alpha_2$, λ = 0.713 59 Å) was used throughout. In each case, the cell constant, a = 12.291 (1) Å for the crystal exposed to Cd vapor and 12.242 (2) Å for the evacuated crystal, was determined by a least-squares treatment of 15 intense reflections for which $20° < 2\theta < 24°$.

For each crystal, reflections from two intensity-equivalent regions of reciprocal space (hkl, $h \le k \le l$, and khl, $k \le h \le l$) were examined using the θ-2θ scan technique. Each reflection was scanned at a constant rate of 1.0 deg min^{-1} from 1° (in 2θ) 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 in diverse regions of reciprocal space were reported after every 100 reflections to monitor crystal and

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Table I. Positional, Thermal,[a] and Occupancy Parameters

	Wyckoff position	x	y	z	β_{11}[b] or B_{iso}[c]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	occupancy factor[d] fixed	occupancy factor[d] varied[e]
					A. $[Cd(H_2O)^{2+}]_3(Cd^+)_3(Cd_2^{2+})_{1.5}$-A							
(Si,Al)	24(*k*)	0	1834(3)	3689(3)	21(3)	20(3)	16(3)	0	0	1(5)	24[f]	24[f]
O(1)	12(*h*)	0	2049(11)	5000[g]	49(13)	51(14)	25(10)	0	0	0	12	12
O(2)	12(*i*)	0	2956(7)	2956(7)	38(12)	25(7)	25(7)	0	0	24(16)	12	12
O(3)	24(*m*)	1128(5)	1128(5)	3314(7)	20(4)	20(4)	64(9)	11(11)	5(9)	5(9)	24	24
Cd(3)	8(*g*)	1537(7)	1537(7)	1537(7)	43(7)	43(7)	43(7)	43(17)	43(17)	43(17)	2.0	1.8(1)
Cd(4)	8(*g*)	1901(3)	1901(3)	1901(3)	29(3)	29(3)	29(3)	16(6)	16(6)	16(6)	3.0	3.2(1)
Cd(5)	8(*g*)	2263(10)	2263(10)	2263(10)	33(7)	33(7)	33(7)	31(15)	31(15)	31(15)	1.0	1.11(6)
Cd(6)	24(*m*)	715(44)	4325(18)	4325(18)	290(98)	122(28)	122(28)	−46(116)	−46(116)	−194(56)	1.0	1.33(7)
Cd(1)	24(*m*)	470[h]	828(24)	828(24)	15(2)						1.0	0.94(6)
Cd(2)	8(g)	1312(13)	1312(13)	1312(13)	1.0(4)						1.0	1.15(8)
O(4)	8(*g*)	2978(34)	2978(34)	2978(34)	9(2)						3.0	4.3(5)
					B. $[Cd(H_2O)^{2+}]_3(Cd^{2+})_3$-A							
(Si,Al)	24(*k*)	0	1826(4)	3681(3)	29(3)	18(4)	29(3)	0	0	10(5)	24[f]	24[f]
O(1)	12(*h*)	0	1976(10)	5000[g]	51(13)	58(14)	49(11)	0	0	0	12	12
O(2)	12(*i*)	0	2950(6)	2950(6)	52(13)	34(7)	34(7)	0	0	29(18)	12	12
O(3)	24(*m*)	1119(4)	1119(4)	3272(6)	48(5)	48(5)	43(8)	13(12)	3(10)	3(10)	24	24
Cd(1)	8(*g*)	1564(3)	1564(3)	1564(3)	54(3)	54(3)	54(3)	34(7)	34(7)	34(7)	3	3.0(3)
Cd(2)	8(*g*)	1955(3)	1955(3)	1955(3)	62(4)	62(4)	62(4)	26(7)	26(7)	26(7)	3	2.8(3)
O(4)	24(*m*)	463(58)	463(58)	800(79)	10.0[h]						3	2.5(2)

[a] Positional and anisotropic thermal parameters are given ×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 2 and 3 for the identities of the atoms. The anisotropic temperature factor = $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] Root mean square displacements can be calculated from β_{ii} values using the formula $\mu_i = 0.225a(\beta_{ii})^{1/2}$. Also, $B_{ii} = 4a^2\beta_{ii}$. [c] Isotropic thermal parameter in units of Å. [d] Occupancy factors are given as the number of atoms or ions per unit cell. [e] See the text for an explanation of this column. [f] Occupancy for (Si) = 12; occupancy for (Al) = 12. [g] Exactly ½, by symmetry. [h] These parameters were held fixed in least-squares refinements.

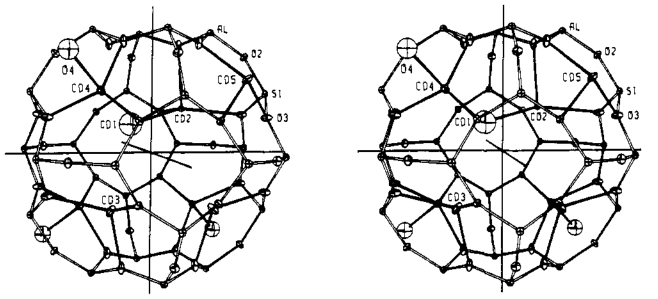

Figure 1. A stereoview[12] of the sodalite unit of Cd_6-A evacuated at 500 °C and then exposed to Cd vapor. Ellipsoids of 20% probability are shown. In this and in the subsequent figures, cadmium ions are arranged within their equipoints of partial occupancy in a chemically plausible manner.

instrument stability. Only small random fluctuations of these check reflections were noted during the course of data collection. All unique reciprocal lattice points (884 and 874 for the Cd-exposed and evacuated crystals, respectively) for which $2\theta < 70°$ were examined. The high upper limit for 2θ was chosen to give a more complete data set, even though few reflections with large 2θ 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.[13] Other details regarding data reduction have been discussed previously.[14] An absorption correction was expected to be unimportant ($\mu R = 0.15$ for the Cd-exposed crystal and 0.09 for the evacuated crystal), and was not applied.[15]

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 303 reflections for the crystal exposed to Cd vapor and 187 for the evacuated crystal.

Structure Determination. Cd_9-A.[16] Full-matrix least-squares refinement was initiated using the atomic parameters of Cd_6-A dehydrated at 600 °C.[4] This model, with the aluminosilicate framework [(Si,Al), O(1), O(2), and O(3)] and two threefold-axis Cd^{2+} ion positions, converged to an R_1 index $(\sum|F_o - |F_c||)/\sum F_o$, of 0.125 and a weighted R_2 index, $(\sum w(F_o - |F_c|)^2/\sum wF_o^2)^{1/2}$, of 0.140. A difference Fourier function at this point revealed many peaks. Four of these, at Cd(5), O(4), Cd(1), and Cd(6) (see Table IA), refined isotropically as approximately 48 e^- at each position, and converged to the error indices $R_1 = 0.112$ and $R_2 = 0.088$. Although the Fourier peak at Cd(1) was at x,z,z, the x coordinate would not refine to a nonzero value. Anisotropic refinement of this atom with x at 0 resulted in a very large β_{11} value of 0.08, so the x coordinate was fixed at 0.047, its value on the difference Fourier function. This atom was refined isotropically in all subsequent least-squares runs. The sodalite-unit Cd^{2+} position from the dehydrated structure was refining as approximately three Cd^{2+} ions, but with an elongated thermal ellipsoid, so it was split into the Cd(2) and Cd(3) positions. Since it was not clear how the position should be split, both models—one with two ions at Cd(2) and one ion at Cd(3) and the other with the occupancies reversed—were tried. The latter resulted in the lower error indices. Up to this point the O(4) position had been refined as Cd,$^{2+}$ since it was not known at the time that the zeolite had not been completely dehydrated prior to the exposure to Cd metal vapor, but its thermal parameter seemed unreasonably large. Attempts to refine it off the threefold axis with a more realistic thermal parameter were unsuccessful, so its identity was changed to oxide, and a more acceptable thermal parameter and comparable R values resulted. Simultaneous positional, occupancy, and thermal parameter refinement was not possible, so occupancy refinement for the nonframework positions was done by fixing positional and varying occupancy and thermal parameters. The results of this refinement are shown in the last column of Table IA. It should be noted that the well-known high correlation between occupancy and thermal parameters limits the utility of such refinements; sometimes unrealistic parameters are generated. The occupancies obtained were revised, by the assumption of stoichiometry and the requirement that the thermal parameters be reasonable and the structure plausible, to the values given for the nonframework positions in the fixed occupancy factor column of Table IA. Anisotropic refinement of all positions, except Cd(1), Cd(2), and O(4), which were refined isotropically, at these fixed occupancies converged with the final error indices $R_1 = 0.079$ and $R_2 = 0.062$. The goodness-of-fit, $(\sum w(F_o - |F_c|)^2/(m - s))^{1/2}$, is 3.19; m (303) is the number of observations, and s (42) is the number of variables in least squares. All shifts in the final cycle of refinement were less than 5% of their corresponding esd's.

The largest peak on the final difference Fourier function, whose

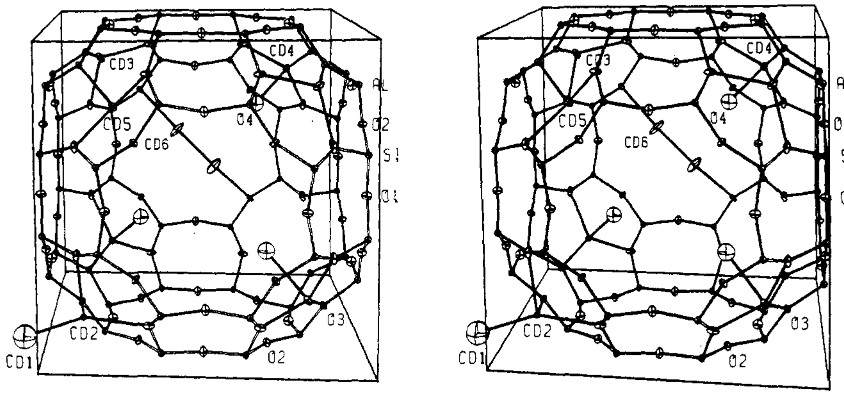

Figure 2. A stereoview[12] of the large cavity of Cd_6-A evacuated at 500 °C and then exposed to Cd vapor. Ellipsoids of 20% probability are shown.

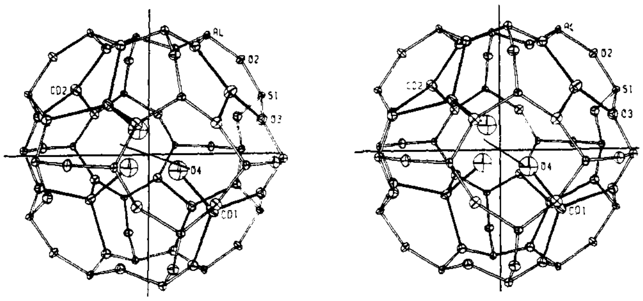

Figure 3. A stereoview[12] of the sodalite unit of Cd_6-A evacuated at 500 °C. Ellipsoids of 20% probability are shown.

estimated standard deviation is 0.12 e Å^{-3} at a general position, was 7.0 e Å^{-3} in height and was located at the origin where the esd is 5.8 e Å^{-3}.

The final structural parameters are presented in Table IA. Interatomic distances and angles are given in Table IIA. See paragraph at end of paper regarding supplementary material. Likely atomic arrangements in a particular unit cell are shown in Figures 1 and 2.

Cd_6-A.[16] Full-matrix least-squares refinement was initiated using the atomic parameters of Cd_6-A dehydrated at approximately 600 °C[4] for the atoms of the aluminosilicate framework [(Si,Al), O(1), O(2), and O(3)] and for two threefold-axis Cd^{2+} ion positions (one in the large cavity and one in the sodalite unit). This model converged quickly to the R values $R_1 = 0.066$ and $R_2 = 0.062$. A subsequent difference Fourier function was essentially flat except for a diffuse region of electron density in the sodalite unit similar to that noted in a previous Cd^{2+}-exchanged crystal, $Cd_{9.5}Cl_4(OH)_3$-A.[17] Least-squares refinement of oxide at O(4) with a thermal parameter fixed at 10.0 and occupancies for the two Cd^{2+} ion positions and for the oxide varying resulted in the error indices $R_1 = 0.057$ and $R_2 = 0.036$ and the occupancies shown in the last column of Table IB. All attempts to refine the thermal parameter, both with and without the occupancy fixed, were unsuccessful, so it was fixed at 10.0 since that was the value found in the aforementioned structure. The occupancies obtained 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 IB. This model converged to the final error indices $R_1 = 0.059$ and $R_2 = 0.039$. The goodness-of-fit is 1.99, the number of observations is 187, and the number of parameters is 29. All shifts in the final cycle of refinement were less than 1% of their corresponding esd's.

The largest peak on the final difference Fourier function, whose estimated standard deviation is 0.082 e Å^{-3} at a general position, was 1.4 e Å^{-3} in height and was located at the origin where the esd is 3.9 e Å^{-3}.

The final structural parameters are presented in Table IB. Interatomic distances and angles are given in Table IIB. A listing of observed and calculated structure factors is available; see paragraph at end of paper regarding supplementary material. A likely atomic arrangement in a particular sodalite unit is shown in Figure 3.

Table II. Selected Interatomic Distances (Å) and Angles (deg)[a]

A. $[Cd(H_2O)^{2+}]_3(Cd^+)_3(Cd_2{}^{2+})_{1.5}$-A			
(Si,Al)-O(1)	1.633(4)	O(1)-(Si,Al)-O(2)	113.8(7)
(Si,Al)-O(2)	1.647(5)	O(1)-(Si,Al)-O(3)	110.5(5)
(Si,Al)-O(3)	1.699(4)	O(2)-(Si,Al)-O(3)	106.2(5)
		O(3)-(Si,Al)-O(3)	109.4(6)
Cd(1)-O(3)	3.18(3)	(Si,Al)-O(1)-(Si,Al)	161.4(6)
Cd(1)-O(3)	3.53(1)	(Si,Al)-O(2)-(Si,Al)	156.3(9)
Cd(1)-Cd(2)	2.35(3)	(Si,Al)-O(3)-(Si,Al)	139.4(6)
Cd(2)-O(3)	2.48(2)		
Cd(3)-O(3)	2.30(1)	O(3)-Cd(2)-O(3)	99.9(7)
Cd(3)-O(2)	3.11(1)	O(3)-Cd(2)-Cd(1)	98.2(8)
Cd(4)-O(3)	2.20(1)	O(3)-Cd(2)-Cd(1)	151.6(9)
Cd(4)-O(2)	2.970(8)	O(3)-Cd(3)-O(3)	111.6(4)
Cd(4)-O(4)	2.29(7)	O(3)-Cd(4)-O(3)	119.8(5)
Cd(5)-O(3)	2.36(1)	O(3)-Cd(4)-O(4)	92.5(8)
Cd(5)-O(2)	3.031(7)	O(3)-Cd(5)-O(3)	107.3(9)
Cd(6)-O(1)	3.05(2)	O(2)-Cd(6)-Cd(6)	160(3)
Cd(6)-O(2)	2.54(4)		
Cd(6)-Cd(6)	2.35(4)		
B. $[Cd(H_2O)^{2+}]_3(Cd^{2+})_3$-A			
(Si,Al)-O(1)	1.625(4)	O(1)-(Si,Al)-O(2)	116.6(6)
(Si,Al)-O(2)	1.641(5)	O(1)-(Si,Al)-O(3)	110.5(4)
(Si,Al)-O(3)	1.696(4)	O(2)-(Si,Al)-O(3)	105.5(5)
		O(3)-(Si,Al)-O(3)	107.7(5)
Cd(1)-O(3)	2.23(1)	(Si,Al)-O(1)-(Si,Al)	167.0(5)
Cd(1)-O(2)	3.070(8)	(Si,Al)-O(2)-(Si,Al)	156.1(8)
Cd(1)-O(4)	2.12(6)	(Si,Al)-O(3)-(Si,Al)	137.5(5)
O(4)-O(4)	2.19(6)		
Cd(2)-O(3)	2.17(1)	O(3)-Cd(1)-O(3)	113.5(3)
Cd(2)-O(2)	2.949(6)	O(3)-Cd(1)-O(4)	96(3)
		O(3)-Cd(1)-O(4)	109(1)
		Cd(1)-O(4)-O(4)	139(5)
		O(3)-Cd(2)-O(3)	118.7(4)

[a] The numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding parameter.

The full-matrix least-squares program[13] used in all structure determinations minimized $\sum w(\Delta|F|)^2$; the weight (w) of an observation was the reciprocal square of σ, its standard deviation. Atomic scattering factors[18,19] for Cd^{2+}, Cd^+, O^-, and $(Si,Al)^{1.75+}$ were used. The function describing $(Si,Al)^{1.75+}$ is the mean of Si^0, Si^{4+}, Al^0, and Al^{3+} functions, and that describing Cd^+ is the mean of Cd^{2+} and Cd^0 functions. The scattering factors for Cd^{2+}, Cd^+, $(Si,Al)^{1.75+}$, and O^- were modified to account for the real component ($\Delta f'$) of the anomalous dispersion correction.[20,21]

Discussion

Cd_9-A. This structure contains 7.5 cadmium species per unit cell (three Cd^{2+}, three Cd^+, and 1.5 $Cd_2{}^{2+}$ ions), and can be described by the formula $[Cd(H_2O)^{2+}]_3(Cd^+)_3(Cd_2{}^{2+})_{1.5}$-A, where each H_2O is likely to have dissociated to form $CdOH^+$

Table III. Deviation of Atoms (Å) from the [111] Plane at O(3)[a]

$[Cd(H_2O)^{2+}]_3(Cd^+)_3$-$(Cd_2{}^{2+})_{1.5}$-A		$[Cd(H_2O)^{2+}]_3$-$(Cd^{2+})_3$-A	
Cd(1)	−2.44	Cd(1)	−0.58
Cd(2)	−1.15	Cd(2)	0.25
Cd(3)	−0.68	O(2)	0.28
Cd(4)	0.09		
Cd(5)	0.87		
O(2)	0.24		

[a] A negative deviation indicates that the atom lies on the same side of the plane as the origin.

and H^+ species. One $Cd_2{}^{2+}$ and two Cd^+ ions are found in the sodalite unit (Figure 1). The $Cd_2{}^{2+}$ ion, with a bond length of 2.35 (3) Å (Table II), is coordinated at Cd(2) to three O(3) framework oxides at 2.48 (2) Å. The other end of the ion at Cd(1) makes two very long approaches (3.18 (3) Å) to two O(3) oxides of an adjacent 6-ring, and an even longer approach (3.53 (1) Å) to the remaining O(3) oxide of that ring. The two Cd^+ ions at Cd(3) are recessed 0.68 Å into the sodalite unit from the O(3) planes of the 6-rings (Table III), and are coordinated to three framework oxides at 2.30 (1) Å.

Three Cd^{2+} ions at Cd(4) are almost in the [111] plane at O(3). They are each coordinated to three framework oxides at O(3) at 2.20 (1) Å and to one oxide (presumably a H_2O molecule which is probably dissociated) in the large cavity at O(4) at 2.29 (7) Å (Figure 2). One Cd^+ ion at Cd(5), also on a threefold axis, extends into the large cavity where it is coordinated at 2.36 (1) Å to three oxides at O(3). The remaining $\frac{1}{2}Cd_2{}^{2+}$ species at Cd(6) is associated with an 8-ring. In contrast to the $Cd_2{}^{2+}$ ion in the sodalite unit, this one is symmetrically coordinated to the framework; each end approaches an O(2) oxide at 2.54 Å. The bond length of 2.35 (4) Å, however, is the same; it appears to be insensitive to the mode of coordination of $Cd_2{}^{2+}$ to the framework.

In this structure, all eight of the 6-rings are occupied by a cadmium species: one each at Cd(1), Cd(2), and Cd(5), two at Cd(3), and three at Cd(4) (Figures 1 and 2). Alternate unit cells also contain a $Cd_2{}^{2+}$ ion at Cd(6) spanning an 8-ring.

The $Cd_2{}^{2+}$ ion bond length, 2.35 Å, is only 0.07 Å (approximately 2σ) longer than the distance obtained by doubling the theoretical univalent ionic radius for Cd^+ (1.14 Å).[22] Doubling the analogous radius for Hg^+ predicts a Hg^+-Hg^+ approach of 2.50 Å, which agrees relatively well with the crystallographically determined bond lengths, which range from 2.41 to 2.54 Å.[5] The monatomic Cd^+ ion to framework oxide approaches are longer (by 0.10 and 0.16 Å) than the Cd^{2+} ion to framework distance, in general agreement with the difference between the radii of Cd^+ and Cd^{2+} (1.14 − 0.97 = 0.17 Å).

The existence of $Cd_2{}^{2+}$ and Cd^+ ions has been reported, but no crystallographic information on these species was heretofore available. Irradiation of aqueous solutions of Cd^{2+} produces highly unstable, strongly reducing monatomic Cd^+ ions.[23] Since cadmium(I) is not stable in aqueous solution, most attempts to study the univalent state have involved the dissolution of cadmium metal in molten cadmium halides.[5] Corbett et al. were able to isolate the diamagnetic compound $Cd_2(AlCl_4)_2$ from such a melt which had been treated with $AlCl_3$.[24] This compound is colorless, as is the zeolite crystal in this investigation.

The relative stability of $Cd_2{}^{2+}$ with respect to the more familiar $Hg_2{}^{2+}$ ion can be seen in the force constants, obtained from Raman spectra, for the two species: 1.1 mdyn Å^{-1} for $Cd_2{}^{2+}$ and 2.5 mdyn Å^{-1} for $Hg_2{}^{2+}$.[25] This greater stability of $Hg_2{}^{2+}$ is attributed to the poor shielding of the 6s electrons by the 4f shell, and the resulting higher electron affinity of Hg^+ relative to Cd^+ (1.4-eV difference).

Sorption of mercury vapor by various zeolites, including Hg-X, has been studied gravimetrically by Barrer and Whiteman.[26] That study indicated that at least some, and possibly all, of the Hg^{2+} ions within the Hg-X were reduced. It was postulated that both dimercury(I) (mercurous) ions and cationic mercury clusters formed; the possibility that monatomic mercury(I) ions formed was not discussed, and is probably unlikely considering the extent of Hg sorption. If Hg-A can be prepared, its Hg sorption complex could be studied crystallographically to clarify the nature of reduced mercury in zeolites. Attempts to prepare the Zn sorption complex of Zn-A are in progress.

Cd_6-A. This structure can be described by the formula $[Cd(H_2O)^{2+}]_3(Cd^{2+})_3$-A, where each H_2O, as in Cd_9-A, is likely to have dissociated. All six Cd^{2+} ions are found on threefold axes (Figure 3). Three are recessed 0.58 Å into the sodalite unit from the O(3) planes of the 6-rings. Each of these Cd^{2+} ions at Cd(1) is coordinated to three O(3) framework oxides at 2.23 (1) Å and to one oxide (presumably a dissociated H_2O molecule) at 2.12 (6) Å in a near-tetrahedral manner. The remaining three Cd^{2+} ions at Cd(2) extend 0.25 Å into the large cavity from the [111] plane at O(3) and are coordinated to three O(3) oxides at 2.17 (1) Å in a slightly distorted trigonal planar arrangement.

The sodalite unit structure is remarkably similar to that found in similarly dehydrated $CdCl_2$-exchanged zeolite A.[17] Both structures involve three Cd^{2+} ions, each coordinated to three framework oxides and to one other oxide at a poorly defined position deeper in the sodalite unit. The O(4)-O(4) distances appear short (2.06 (7) Å in $Cd_{9.5}Cl_4(OH)_3$-A and 2.19 (6) Å in this structure) and are perhaps due to very strong hydrogen bonding, but the problems encountered in the refinement of this position leave the details of the O(4) position (both the coordinates and the symmetry) unresolved, and make interpretation difficult.

Zn_5K_2-A evacuated at 400 °C contains 3.5 water molecules per unit cell.[27] Each of these H_2O molecules (presumably dissociated) is coordinated to a Zn^{2+} ion, which is also coordinated to three framework oxides, and completes a tetrahedral coordination sphere around the cation. Although the arrangement of residual water molecules in that structure is not the same as in Cd_6-A, the tenacity with which the last few H_2O molecules are held is similar.

Dipositive ions do not balance the anionic charge of the aluminosilicate framework as evenly as would a greater number of monopositive ions. Zn^{2+} and Cd^{2+}, unlike the alkaline-earth cations, are capable of hydrolyzing H_2O (pK_h ca. 9 for Zn^{2+} and 10 for Cd^{2+}).[28] Consequently, partially dehydrated Zn_5K_2-A and Cd_6-A probably contain protons associated with framework oxides, and MOH^+ species (M = Zn or Cd), and therefore complete dehydration of these zeolites is difficult. Such reasoning would explain why other dipositive-ion forms of zeolite A which have been studied crystallographically have been completely dehydrated: the cations in Ca_6-A, Sr_6-A,[29] and Eu_xNa_{12-2x}-A[30] cannot hydrolyze water to any appreciable extent,[28] and Co_4Na_4-A,[31] $Mn_{4.5}Na_3$-A,[32] and $Cd_{9.5}Cl_4(OH)_3$-A[17] may contain a sufficient number of cationic species to satisfy charge distribution requirements.

Other Discussion. The fact that the positions of the framework oxides are only average positions must be borne in mind when considering cadmium to framework oxide approaches. Although there are five chemically different 6-rings in the Cd_9-A structure, and three in the Cd_6-A one, only a single, average O(3) position is used to describe the framework oxides at O(3) in each case. Cd(II) ions can cause these framework oxides to buckle inward toward the center, while Cd(I) ions should cause a much smaller ring deformation. Thus, the actual Cd(II)-O(3) distances should be somewhat shorter than those observed, and the Cd(I)-O(3) distances longer. Similar averaging of the O(2) position in Cd_9-A may be expected to modify the Cd(6)-O(2) approach distance also.

Although only average O(3) positions have been found in both Cd_9-A and Cd_6-A, the (Si,Al)-O(3) distances (also averages) in both structures are significantly longer than the (Si,Al)-O(1) and (Si,Al)-O(2) distances. Eight of the nine cadmium species in Cd_9-A and all six of those in Cd_6-A are associated with O(3) oxides, and consequently the (Si,Al)-O(3) bond has been weakened and lengthened. This effect has been observed and discussed previously.[29]

The observation that three H_2O molecules are retained even after Cd_6-A is evacuated at 500 °C allows for a relatively simple explanation of the end point reached in its cadmium sorption complex. In order to relieve its state of coordinative unsaturation, each three-coordinate Cd^{2+} ion has reacted with a Cd^0 atom to form Cd(I), either as Cd^+ or Cd_2^{2+}; the three four-coordinate Cd^{2+} ions do not react with Cd^0. It might be expected that, if Cd_6-A could be completely dehydrated, all six Cd^{2+} ions would react with Cd^0 to give a structure with 12 cadmiums (possibly even more) per unit cell.

Cd_2^{2+} appears to prefer a site in the sodalite unit, which is large enough to accommodate only one such ion. If more Cd were sorbed to generate more Cd(I), the occupancy of Cd_2^{2+} at the 8-ring sites would be expected to increase.

Cadmium(I) should be a strong reducing agent, whether mono- or binuclear, and within a zeolite it may have unique chemical properties. Cadmium zeolite systems may be interesting catalysts or reagents.

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Supplementary Material Available: Listings of the observed and calculated structure factors for both structures (Supplementary Tables 1 and 2) (3 pages). Ordering information is given on any current masthead page.

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(16) The abbreviated notation Cd_9-A and Cd_6-A will be used throughout to refer to the Cd-exposed ($[Cd(H_2O)^{2+}]_3(Cd^+)_3(Cd_2^{2+})_{1.5}$-A) and the evacuated ($[Cd(H_2O)^{2+}]_3(Cd^{2+})_3$-A) structures, respectively.

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