Crystal Structures of Vacuum Dehydrated Fully Cd^{2+} – Exchanged Zeolite A and Its Ethylene Sorption Complex

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The crystal structure of dehydrated fully Cd^{2+}-exchanged zeolite A evacuated at 2×10^{-6} Torr and 450℃ (a = 12.225(2) Å) and of its ethylene sorption complex (a = 12.219(2) Å) have been determined by single crystal X-ray diffraction techniques in the cubic space group $Pm3m$ at 21(1)℃. The structures were refined to final error indices, R_1 = 0.063 and R_2 = 0.065 with 266 reflections and R_1 = 0.055 and R_2 = 0.062 with 260 reflections, respectively, for which $I>3\sigma(I)$. In both structures, six Cd^{2+} ions lie at two distinguished three-fold axes of unit cell. Dehydrated Cd_6-A sorbs 4 ethylene molecules per unit cell at 25℃ (vapor pressure of ethylene is *ca.* 100 Torr). Each Cd^{2+} ion forms a lateral π complex with an ethylene molecule. Four Cd^{2+} ions exist in a nearly tetrahedral environment, 2.210(7) Å apart from three framework oxygen ions (considering ethylene molecule as a monodentate ligand) and 2.67(6) Å from each carbon atom of ethylene molecule.

Introduction

The transition metal ions which have been ion exchanged into zeolites are very often unusually coordinated or coordinately unsaturated. As a result, they have unusual chemical properties. The zeolite framework, in contrast to the conventional complexing ligands, does not conform to the geometrical requirement of the metal ions to form stable complexes. The metal ions must choose their positions among the various available sites in zeolite, using water or other guest molecules if available, to achieve the most favorable coordination state. Removal of water upon dehydration can result in coordinative unsaturation.

All Mn(II) ions in the hydrated form of partially Mn(II)-exchanged zeolite A are found to have nearly regular trigonal bipyramidal coordination with water molecules in the axial positions and three equivalent framework oxygen atoms arranged equatorially.[1] Upon dehydration, the Mn(II) ions are found to be three coordinate, with a near trigonal-planar geometry. Co(II) ion in dehydrated partially Co(II)-exchanged zeolite A has nearly the same trigonal planar coordination. Three-coordinate metal ions are unusual and should tend to increase their coordination numbers by forming complexes with a variety of guest molecules introduced under vacuum techniques.[2]

Carter *et al.* have studied the sorption of ethylene at room temperature onto a series of ion-exchanged synthetic near-faujasites by infrared spectroscopy and by microcalorimetry.[3] They found that C_2H_4 molecules form laterally held complexes of symmetry C_2. Of the transition metal ions examined, Ag^+ and Cd^{2+} were found to hold C_2H_4 most strongly. Furthermore, the adsorbed ethylene molecule is reported to be freely rotating in all the cases, except for their Ag^+ and Cd^{2+} complexes.

Crystal structure of vacuum dehydrated Cd(II) exchanged-zeolite A has been determined previously with a small data set of 187 reflections. In this structure, three 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 they are coordinated to three framework oxygens and a fourth oxide in a near-tetrahedral manner.[4]

The crystal structure of an ethylene sorption complex of partially decomposed fully Ag^+-exchanged zeolite A has been determined.[5] In this structure, *ca.* 3.8 Ag^+ ions per unit cell are recessed approximately 1.2 Å into the large zeolite cavity where each forms lateral π complex with an ethylene molecule. These Ag^+ ions exist in a nearly tetrahedral environment, 2.49(1) Å from three framework oxide ions and 2.54(8) Å from each carbon atom of an ethylene molecules(C-C = 1.19 (12) Å).

To further investigate the interesting sorption properties of zeolite A, the crystal structures of the vacuum dehydrated fully Cd^{2+}-exchanged zeolite A and its ethylene sorption complex have been determined by single crystal X-ray diffraction techniques.

Experimetal Section

Crystals of zeolite 4A were prepared by Charnell's method,[6] modified by the inclusion of seed crystals from a previous preparation. A single crystal about 0.085 mm on an edge was selected and lodged in a fine capillary. To prepare fully Cd^{2+}-exchanged zeolite A, an exchange solution of $Cd(NO_3)_2$ and $Cd(OOCCH_3)_2$ in the molar ratio of 1:1, with total concentration of 0.05 M, was used. Ion exchange was accomplished by allowing the solution to flow past each crystal at a velocity of approximately 0.5 cm/s for *3d* at 25℃. These crystals were washed for 1 h with distilled water at 80℃. The clear, colorless, hydrated Cd^{2+}-exchanged crystal was dehydrated for *2d* at 450℃ and 2×10^{-6} Torr. To prepare the ethylene complex, the crystal was treated with 100 Torr of zeolitically dried ethylene for 1 h at 25℃. The resulting reddish yellow crystal, still in its ethylene atmosphere, was sealed in its capillary by a torch.

The cubic space group $Pm3m$(no systematic absence) was used instead of $Fm3c$ for reasons described previously.[7,8] Preliminary crystallographic experiments and subsequent data collection were performed with an automated, four-circle Enraf Nonius CAD-4 diffractometer equipped with graphite

Table 1. Positional, Thermal, and Occupancy Parameters for the Dehydrated Cd_6-A and its Ethylene Sorption Complexes

(a) Crystal 1, Vacuum Dehydrated Cd_6-A[a]

Atom	Wyc. pos.	x	y	z	[b]β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	[c]Occupancy varied	fixed
(Si, Al)	24(*k*)	0	1827(3)	3682(3)	23(2)	20(2)	19(2)	0	0	8(4)		24.00
O(1)	12(*h*)	0	2000(10)	5000	60(10)	50(10)	36(9)	0	0	0		12.00
O(2)	12(*i*)	0	2952(7)	2952(7)	38(9)	31(5)	31(5)	0	0	50(10)		12.00
O(3)	24(*m*)	1117(3)	1117(3)	3271(6)	37(4)	37(4)	36(7)	10(10)	18(8)	18(8)		24.00
Cd(1)	8(*g*)	1944(4)	1944(4)	1944(4)	44(1)	44(1)	44(1)	37(3)	37(3)	37(3)	2.59(3)	
Cd(2)	8(*g*)	1575(2)	1575(2)	1575(2)	61(2)	61(2)	61(2)	53(5)	53(5)	53(5)	3.42(3)	

(b) Crystal 2, Ethylene Sorption Complexes of Cd_6-A

Atom	Wyc. pos.	x	y	z	[b]β_{11} β_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	[c]Occupancy varied	fixed
(Si, Al)	24(*k*)	0	1822(3)	3680(2)	28(2)	19(1)	14(1)	0	0	4(3)		24.00
O(1)	12(*h*)	0	2020(10)	5000	80(10)	49(9)	24(7)	0	0	0		12.00
O(2)	12(*i*)	0	2964(7)	2964(7)	48(8)	35(4)	35(4)	0	0	4(2)		12.00
O(3)	24(*m*)	1122(5)	1122(5)	3279(5)	36(3)	36(3)	50(6)	10(9)	−9(7)	−9(7)		24.00
Cd(1)	8(*g*)	2079(2)	2079(2)	2079(2)	47(1)	47(1)	47(1)	16(3)	16(3)	16(3)	3.7(1)	4.0
Cd(2)	8(*g*)	1553(4)	1553(4)	1553(4)	50(2)	50(2)	50(2)	50(5)	50(5)	50(5)	1.9(1)	2.0
C(1)	48(*n*)	2960(50)	3240(60)	3700(40)	8(2)[d]						8.8(7)	8.0

[a]Positional and anisotropic thermal parameters are given × 10^4. Numbers in parentheses are the esd's in the units of the least significant digit given for the corresponding parameter. [b]The anisotropic temperature factor-$\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$. Rms displacements can be calculated from β_{ij} values by using the formula $u_i=0.225\ a(\beta_{ij})^{1/2}$, where $a=12.225(2)$ Å for Cd_6-A and $a=12.219(2)$ Å for ethylene sorption structure. [c]Occupancy factors are given as the number of atoms or ions per unit cell. Occupancy for (Si) = 12; [d]Occupancy for (Al) = 12. [e]This thermal parameter was calculated as the occupancy parameter fixed (Isotropic thermal parameter is in units of $Å^2$).

monochromator and PDP micro 11/73 computer. Mo K_α radiation($K_{\alpha 1}$, $\lambda=0.70930$ Å; $K_{\alpha 2}$, $\lambda=0.71359$ Å) was used for all experiments. The unit cell constant, as determined by a least-squares refinement of 25 intense reflections for which $19° < 2\theta < 24°$ are 12.225(2) Å for Cd_6-A and 12.219(2) Å for its ethylene sorption complex, respectively.

For each crystal, reflections from two intensity-equivalent regions of reciprocal space($h\ k\ l$, $h \leq k \leq l$ and $l\ k\ h$, $l \leq k \leq h$) were examined using ω-2θ scan technique. The data were collected by using variable scan speeds. Most reflections were observed at the slow scan speeds, from 0.25 to 0.31 deg min^{-1} in ω. The intensities of three reflections in diverse regions of reciprocal space were recorded after every three hours to monitor crystal and X-ray source stability. Only small, random fluctuations of these check reflections were noted during the course of data collection. For each region of reciprocal space, the intensities of all lattice points for which $2\theta < 70°$ were recorded. The intensities were corrected for Lorentz and polarization effects; the contribution of the monochromatic crystal was calculated, assuming it to be half perfect and half-mosaic in character.[9]

An absorption correction($\mu = 2.13$ mm^{-1} for Cd_6-A and $\mu = 2.14$ mm^{-1} for ethylene sorption complex of Cd_6-A) was judged to be negligible and was not applied.[10]

Of the 867 pairs of reflections for the crystal of Cd_6-A and 864 pairs for the crystal of ethylene sorption complex of Cd_6-A, only 266 and 260 pairs, respectively, for which $I > 3\sigma(I)$ were used in subsequent structure determinations.

Full-matrix least-squares refinement of the dehydrated Cd_6-A was initiated by using the atomic parameters of the framework atoms ((Si, Al)), O(1), O(2), and O(3)) in dehydrated Ag^+ exchanged zeolite A treated with CO molecules.[11] Anisotropic refinement of the framework atoms converged to an R_1 index, $(\Sigma(\mid F_o - \mid F_c \mid \mid)/\Sigma F_o)$, of 0.430 and a weighted R_2 index, $(\Sigma\omega(F_o - \mid F_c \mid)^2/\Sigma\omega F_o^2)^{1/2}$, of 0.488. From the initial difference Fourier function, Cd^{2+} ions at Cd(1) and Cd(2) were readily located(see Table 1) and refined. Anisotropic refinement including these Cd^{2+} ions at Cd(1) and Cd (2) positions coverged to $R_1 = 0.063$ and $R_2 = 0.065$. The final difference Fourier map was featureless.

The initial structural parameters used in the least-squares refinement for ethylene sorption complexes were those previously found for Cd^{2+} ions at Cd(1) and Cd(2), (Si, Al), O(1), O(2), and O(3) positions in the structure of dehydrated Cd_6-A. Anisotropic refinement of this structure model converged to $R_1 = 0.081$ and $R_2 = 0.092$.

A successive difference Fourier map indicated that the carbon atoms of the ethylene molecules appeared at the 48 fold position (0.310, 0.330, 0.360) with a peak height of 1.1(2) $eÅ^{-3}$. This corresponds closely to the final result, that approximately 8.0 carbon atoms are found very near to this position. It was assumed that one C_2H_4 molecule is associated with each Cd^{2+} ion at Cd(1), such coordination being reason that Cd^{2+} ion at Cd(1) recessed approximately 0.504(1) Å into the large cavity at a near tetrahedral 4-coordinate position. Refinement of about eight carbon atoms per unit cell

Table 2. Selected Interatomic Distances(Å) and Angles(deg)

	Crystal 1	Crystal 2
(Si, Al)-O(1)	1.624(4)	1.631(3)
(Si, Al)-O(2)	1.640(8)	1.646(8)
(Si, Al)-O(3)	1.694(5)	1.688(5)
Cd(1)-O(3)	2.162(7)	2.210(6)
Cd(2)-O(3)	2.219(7)	2.236(7)
Cd(1)-C(1)		2.67(6)
C(1)-C(1)		1.27(8)
O(1)-(Si, Al)-O(2)	115.6(5)	113.6(5)
O(1)-(Si, Al)-O(3)	111.1(4)	111.3(5)
O(2)-(Si, Al)-O(3)	105.5(2)	106.0(2)
O(3)-(Si, Al)-O(3)	107.4(3)	108.6(3)
(Si, Al)-O(1)-(Si, Al)	165.2(9)	163.1(9)
(Si, Al)-O(2)-(Si, Al)	156.0(4)	154.2(4)
(Si, Al)-O(3)-(Si, Al)	137.6(4)	137.6(4)
O(3)-Cd(1)-O(3)	118.9(2)	115.0(2)
O(3)-Cd(2)-O(3)	114.1(2)	112.9(2)
O(3)-Cd(1)-O(1)		90(1)
Cd(1)-C(1)-C(1)		78(5)

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

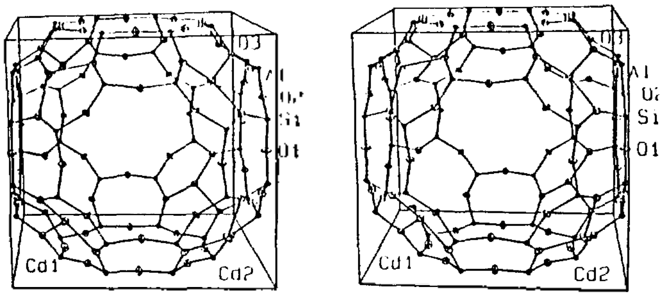

Figure 1. The stereoview of large cavity of vacuum dehydrated Cd_6-A. 3 Cd^{2+} ions at Cd(1) and 3 Cd^{2+} ions at Cd(2) are shown. Almost 60% of unit cell may have this stoichiometry. Ellipsoids of 20% probability are shown.

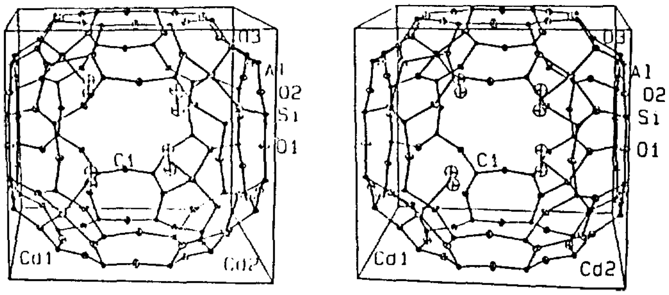

Figure 2. The stereoview of large cavity of vacuum dehydrated Cd_6-A treated with C_2H_4. The hydrogen atoms, whose positions were not determined, are not shown. Four ethylene molecules are coordinated to each Cd^{2-} ion at Cd(1). Ellipsoids of 20% probability are used.

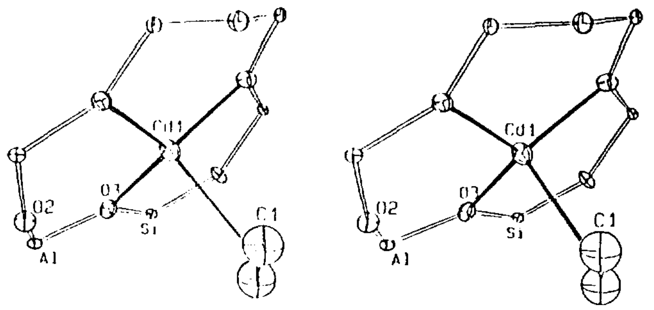

Figure 3. A stereoview of Cd(II)-C_2H_4 complex in one corner of the large cavity. The approximately tetrahedral coordination about Cd^{2+} can be seen. The hydrogen atoms, whose positions were not determined, are not shown. Ellipsoids of 20% probability are used.

at this position, constrained to be no more than twice the number of Cd^{2+} ions at Cd(1), converged readily. At final convergence, $R_1 = 0.055$ and $R_2 = 0.062$ for ethylene sorption complex of Cd_6-A.

The full-matrix least-squares program used in all structure determinations minimized $\Sigma\omega(F_o - |F_c|)^2$; the weight ($w$) of an observation was the reciprocal square of $\sigma(F_o)$, its standard deviation. Atomic scattering factors[12,13] for C, Cd^{2+}, O^-, and $(Si, Al)^{1.75+}$ were used. The function describing $(Si, Al)^{1.75+}$ is the mean of the Si^0, Si^{4+}, Al^0, and Al^{3+} functions. All scattering factors were modified to account for anomalous dispersion.[14] The final structural parameters are presented in Table 1. Interatomic distances and angles are given in Table 2.

Discussion

In the crystal structure of vacuum dehydrated Cd_6-A, all six Cd^{2+} ions are found on two distinguished three fold axes (Table 1 and Figure 1). About 2.6 Cd^{2+} ions at Cd(1) extended 0.23 Å into the large cavity from the (111) plane at O(3) and are coordinated to three O(3) oxygens at 2.162(7) Å in a slightly distorted trigonal planar arrangement. About 3.4 Cd^{2+} ions at Cd(2) are recessed 0.55 Å into the sodalite unit from the O(3) planes of the 6-ring. Each of these Cd^{2+} ions at Cd(2) is coordinated to three O(3) framework oxygens at 2.219(7) Å. Although only average O(3) positions have been found in the present structural studies, 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.

All six of Cd^{2+} ions are associated with O(3) oxygens and consequently the (Si, Al)-O(3) bond has been weakened and lengthened. This effect has also been observed and discussed previously.[15]

The fractional occupancies observed at Cd(1) and Cd(2) indicate the existence of approximately two types of unit cell. For example, about 60% of the unit cells may have 3 Cd^{2+} ions at Cd(1) and 3 Cd^{2+} ions at Cd(2), and the remaining 40% would have 2 Cd^{2+} ions at Cd(1) and 4 Cd^{2+} ions at Cd(2).

To coordinate to ethylene, the ions at Cd(1) have moved 0.272 Å further into the large cavity (see Figures 1 and 3) and away from their triads of three O(3) oxides ions to more tetrahedral coordination situation(considering ethylene to be

Table 3. Deviations of Atoms(Å) from the (111) Plane at O(3)

	Crystal 1	Crystal 2
O(2)	0.282(5)	0.286(5)
Cd(1)	0.232(2)	0.504(1)
Cd(2)	−0.550(2)	−0.609(3)

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

monodentate).

The length of the Cd(1)-O(3) bond has increased from 2.162(7) Å in the vacuum-dehydrated structure to 2.210(6) Å in ethylene sorption structure. Also the O(3)-Cd(1)-O(3) bond angle changes from a near trigonal planar value of 118.9(2)° in vaccum-dehydrated Cd_6-A to 115.0(2)° in ethylene complex, a value closer to tetrahedral. Figures 2 and 3 illustrate the coordination environment of the Cd^{2+} ions. The length of the Ag^+-O^{2-} bonds have increased from 2.25 Å in dehydrated Ag_{12}-A compared to 2.49(1) Å in ethylene sorption complexes.[3] The O(3)-Ag^+-O(3) bond angles have decreased from a nearly planar value, 119.6(4)° in dehydrated Ag_{12}-A to 98.1(4)° for ethylene sorption complexes.

Because of the combined effects of disorder(the averaging of Al and Si positions into a single (Si, Al) position and of the oxide ion positions as though the coordination spheres of Si and Al were the same size) and moderately high thermal motions, the ethylenic double bond length (1.27(8) Å) is a little bit shorter and inaccurately determined. This result is very similar to those found in the ethylene sorption complexes of Co_4Na_4-A[16] 1.21(11) Å and that of Ag_{12}-A,[5] 1.19(12) Å 1.19(12) Å. For comparison, the C-C bond length in ethylene gas is 1.334 Å.[17]

The bonding between the Cd^{2+} ion at Cd(1) and ethylene can be described in terms of two components according to the Chatt Dewar model.[18] A σ component arises from the overlap of a filled ethylene orbital and a vacant Cd^{2+} 5*s* orbital and a π component occurs by the overlap of the filled 4*d* orbitals of Cd^{2+} with the vacant antibonding π^* orbital of ethylene. Due to the latter interaction, the C-C bond order may be diminished somewhat by back donation. It is possible that the difference between cadmium and silver in their ability to back-donate 4*d* electrons to the π^* orbital of ethylene lies in their difference in ionic radii. Cadmium, a divalent ion, has an ionic radius of 0.98 Å, compared to 1.26 Å for the monovalent silver.[19] This suggests that the filled 4*d* orbitals of Cd^{2+} ion do not reach sufficiently far out in space to effectively, whereas types of silver do. The Cd^{2+} ion can not form an effective back bonding with ethylene because its *d* orbital are probably too contracted. The Ag^+-C distance, 2.54 Å in Ag^+-ethylene sorption complexes of Ag^+-A is shorter than the present Cd^{2+}-C distance, 2.67(6) Å[5]. Therefore Cd^{2+}-C_2H_4 complexes in zeolite A have a little weaker interaction than Ag^+-C_2H_4 complexes.

Carter *et al.*[3] studied the sorption of ethylene by a series of transition metal ion exchanged zeolite X samples using calorimetric and IR methods. They found that ethylene is relatively weakly held and that it can be readily removed by evacuation at room temperature, unless the ion involved is Ag^+ or Cd^{2+}. The Cd(1)-C bond length, herein reported as 2.67(6) Å indicates that ethylene is moderately interacted with the Cd^{2+} ion at Cd(1).

Although there is some uncertainties in carbon positions and the determination of the C-C bond distances is not accurate, it is still clear that the ethylene molecules make no significant approaches to the zeolite framework. The closest C-O approach distance is 3.47 Å to O(3) ion(see Figures 2 and 3). The hydrogen atoms would therefore be too far from the nearest oxide ions to interact with them, even if the C-H-O angle was linear. Since the energy of the interaction between ethylene and Cd^{2+} is not considered great enough to cause an appreciable deviation of the hydrogen atoms from the best ethylene plane, C-H-O should be bent (see Figure 3) and the hydrogen should be far, more than 2.0 Å from the nearest oxide neighbors.

Acknewledgement. The present studies were supported in part by the Basic Research Institute program, Ministry of Education, 1990, project No. BSRI-90-020.

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