

## Crystal Structures of Vacuum Dehydrated Fully Cd<sup>2+</sup>-Exchanged Zeolite A and Its Ethylene Sorption Complex

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The crystal structure of dehydrated fully Cd<sup>2+</sup>-exchanged zeolite A evacuated at  $2 \times 10^{-6}$  Torr and 450°C ( $a = 12.225(2)$  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  $Pm\bar{3}m$  at 21(1)°C. 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<sup>2+</sup> ions lie at two distinguished three-fold axes of unit cell. Dehydrated Cd<sub>6</sub>-A sorbs 4 ethylene molecules per unit cell at 25°C (vapor pressure of ethylene is ca. 100 Torr). Each Cd<sup>2+</sup> ion forms a lateral  $\pi$  complex with an ethylene molecule. Four Cd<sup>2+</sup> 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.<sup>1</sup> 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.<sup>2</sup>

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.<sup>3</sup> They found that C<sub>2</sub>H<sub>4</sub> molecules form laterally held complexes of symmetry C<sub>2</sub>. Of the transition metal ions examined, Ag<sup>+</sup> and Cd<sup>2+</sup> were found to hold C<sub>2</sub>H<sub>4</sub> most strongly. Furthermore, the adsorbed ethylene molecule is reported to be freely rotating in all the cases, except for their Ag<sup>+</sup> and Cd<sup>2+</sup> 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<sup>2+</sup> 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<sup>2+</sup> ions are recessed into the sodalite

unit, where they are coordinated to three framework oxygens and a fourth oxide in a near-tetrahedral manner.<sup>4</sup>

The crystal structure of an ethylene sorption complex of partially decomposed fully Ag<sup>+</sup>-exchanged zeolite A has been determined.<sup>5</sup> In this structure, ca. 3.8 Ag<sup>+</sup> ions per unit cell are recessed approximately 1.2 Å into the large zeolite cavity where each forms lateral  $\pi$  complex with an ethylene molecule. These Ag<sup>+</sup> 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<sup>2+</sup>-exchanged zeolite A and its ethylene sorption complex have been determined by single crystal X-ray diffraction techniques.

### Experimental Section

Crystals of zeolite 4A were prepared by Charnell's method,<sup>6</sup> 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<sup>2+</sup>-exchanged zeolite A, an exchange solution of Cd(NO<sub>3</sub>)<sub>2</sub> and Cd(OOCCCH<sub>3</sub>)<sub>2</sub> 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°C. These crystals were washed for 1 h with distilled water at 80°C. The clear, colorless, hydrated Cd<sup>2+</sup>-exchanged crystal was dehydrated for 2d at 450°C and  $2 \times 10^{-6}$  Torr. To prepare the ethylene complex, the crystal was treated with 100 Torr of zeolitically dried ethylene for 1 h at 25°C. The resulting reddish yellow crystal, still in its ethylene atmosphere, was sealed in its capillary by a torch.

The cubic space group  $Pm\bar{3}m$  (no systematic absence) was used instead of  $Fm\bar{3}c$  for reasons described previously.<sup>7,8</sup> 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<sub>6</sub>-A and its Ethylene Sorption Complexes(a) Crystal 1, Vacuum Dehydrated Cd<sub>6</sub>-A<sup>a</sup>

Atom	Wyc. pos.	x	y	z	<sup>b</sup> β <sub>11</sub>	β <sub>22</sub>	β <sub>33</sub>	β <sub>12</sub>	β <sub>13</sub>	β <sub>23</sub>	Occupancy	
											varied	fixed
(Si, Al)	24( <i>k</i> )	0	1827(3)	3682(3)	23(2)	20(2)	19(2)	0	0	8(4)		24.00
O(1)	12( <i>h</i> )	0	2000(10)	5000	60(10)	50(10)	36(9)	0	0	0		12.00
O(2)	12( <i>i</i> )	0	2952(7)	2952(7)	38(9)	31(5)	31(5)	0	0	50(10)		12.00
O(3)	24( <i>m</i> )	1117(3)	1117(3)	3271(6)	37(4)	37(4)	36(7)	10(10)	18(8)	18(8)		24.00
Cd(1)	8( <i>g</i> )	1944(4)	1944(4)	1944(4)	44(1)	44(1)	44(1)	37(3)	37(3)	37(3)	2.59(3)	
Cd(2)	8( <i>g</i> )	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<sub>6</sub>-A

Atom	Wyc. pos.	x	y	z	<sup>b</sup> β <sub>11</sub>	β <sub>22</sub>	β <sub>33</sub>	β <sub>12</sub>	β <sub>13</sub>	β <sub>23</sub>	Occupancy	
											varied	fixed
(Si, Al)	24( <i>k</i> )	0	1822(3)	3680(2)	28(2)	19(1)	14(1)	0	0	4(3)		24.00
O(1)	12( <i>h</i> )	0	2020(10)	5000	80(10)	49(9)	24(7)	0	0	0		12.00
O(2)	12( <i>i</i> )	0	2964(7)	2964(7)	48(8)	35(4)	35(4)	0	0	4(2)		12.00
O(3)	24( <i>m</i> )	1122(5)	1122(5)	3279(5)	36(3)	36(3)	50(6)	10(9)	-9(7)	-9(7)		24.00
Cd(1)	8( <i>g</i> )	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( <i>g</i> )	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( <i>n</i> )	2960(50)	3240(60)	3700(40)	8(2) <sup>d</sup>						8.8(7)	8.0

<sup>a</sup>Positional and anisotropic thermal parameters are given  $\times 10^4$ . Numbers in parentheses are the esd's in the units of the least significant digit given for the corresponding parameter. <sup>b</sup>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  $\beta_{ij}$  values by using the formula  $u_i = 0.225 a(\beta_{ij})^{1/2}$ , where  $a = 12.225(2)$  Å for Cd<sub>6</sub>-A and  $a = 12.219(2)$  Å for ethylene sorption structure. <sup>c</sup>Occupancy factors are given as the number of atoms or ions per unit cell. Occupancy for (Si)=12; <sup>d</sup>Occupancy for (Al)=12. <sup>e</sup>This thermal parameter was calculated as the occupancy parameter fixed (Isotropic thermal parameter is in units of Å<sup>2</sup>).

monochromator and PDP micro 11/73 computer. Mo  $K_{\alpha}$  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  $19^\circ < 2\theta < 24^\circ$  are  $12.225(2)$  Å for Cd<sub>6</sub>-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  $\omega$ - $2\theta$  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  $\text{min}^{-1}$  in  $\omega$ . 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  $2\theta < 70^\circ$  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.<sup>9</sup>

An absorption correction ( $\mu = 2.13$   $\text{mm}^{-1}$  for Cd<sub>6</sub>-A and  $\mu = 2.14$   $\text{mm}^{-1}$  for ethylene sorption complex of Cd<sub>6</sub>-A) was judged to be negligible and was not applied.<sup>10</sup>

Of the 867 pairs of reflections for the crystal of Cd<sub>6</sub>-A and 864 pairs for the crystal of ethylene sorption complex of Cd<sub>6</sub>-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<sub>6</sub>-A was initiated by using the atomic parameters of the framework atoms ((Si, Al), O(1), O(2), and O(3)) in dehydrated Ag<sup>+</sup> exchanged zeolite A treated with CO molecules.<sup>11</sup> Anisotropic refinement of the framework atoms converged to an  $R_1$  index,  $(\sum(|F_o| - |F_c|)|)/\sum F_o$ , of 0.430 and a weighted  $R_2$  index,  $(\sum \omega(F_o - |F_c|)^2 / \sum \omega F_o^2)^{1/2}$ , of 0.488. From the initial difference Fourier function, Cd<sup>2+</sup> ions at Cd(1) and Cd(2) were readily located (see Table 1) and refined. Anisotropic refinement including these Cd<sup>2+</sup> ions at Cd(1) and Cd(2) positions converged 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<sup>2+</sup> ions at Cd(1) and Cd(2), (Si, Al), O(1), O(2), and O(3) positions in the structure of dehydrated Cd<sub>6</sub>-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<sup>-3</sup>. 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<sub>2</sub>H<sub>4</sub> molecule is associated with each Cd<sup>2+</sup> ion at Cd(1), such coordination being reason that Cd<sup>2+</sup> 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.

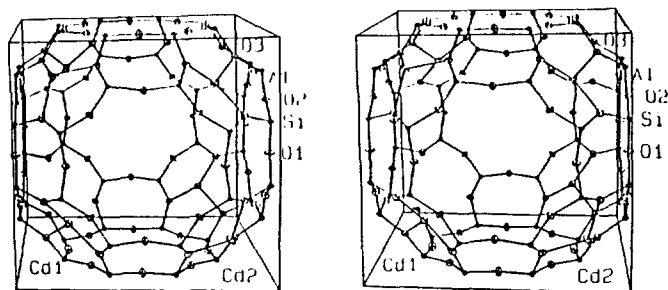
at this position, constrained to be no more than twice the number of  $\text{Cd}^{2+}$  ions at Cd(1), converged readily. At final convergence,  $R_1=0.055$  and  $R_2=0.062$  for ethylene sorption complex of  $\text{Cd}_6\text{-A}$ .

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

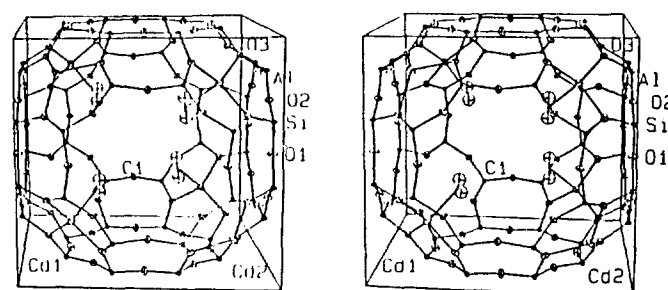
## Discussion

In the crystal structure of vacuum dehydrated  $\text{Cd}_6\text{-A}$ , all six  $\text{Cd}^{2+}$  ions are found on two distinguished three fold axes (Table 1 and Figure 1). About 2.6  $\text{Cd}^{2+}$  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  $\text{Cd}^{2+}$  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  $\text{Cd}^{2+}$  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.

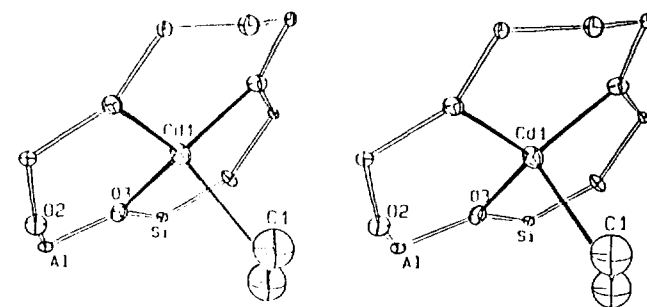
All six of  $\text{Cd}^{2+}$  ions are associated with O(3) oxygens and consequently the (Si, Al)-O(3) bond has been weakened and



**Figure 1.** The stereoview of large cavity of vacuum dehydrated  $\text{Cd}_6\text{-A}$ . 3  $\text{Cd}^{2+}$  ions at Cd(1) and 3  $\text{Cd}^{2+}$  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  $\text{Cd}_6\text{-A}$  treated with  $\text{C}_2\text{H}_4$ . The hydrogen atoms, whose positions were not determined, are not shown. Four ethylene molecules are coordinated to each  $\text{Cd}^{2+}$  ion at Cd(1). Ellipsoids of 20% probability are used.



**Figure 3.** A stereoview of  $\text{Cd(II)-C}_2\text{H}_4$  complex in one corner of the large cavity. The approximately tetrahedral coordination about  $\text{Cd}^{2+}$  can be seen. The hydrogen atoms, whose positions were not determined, are not shown. Ellipsoids of 20% probability are used.

lengthened. This effect has also been observed and discussed previously.<sup>15</sup>

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  $\text{Cd}^{2+}$  ions at Cd(1) and 3  $\text{Cd}^{2+}$  ions at Cd(2), and the remaining 40% would have 2  $\text{Cd}^{2+}$  ions at Cd(1) and 4  $\text{Cd}^{2+}$  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 vacuum-dehydrated Cd<sub>5</sub>-A to 115.0(2)° in ethylene complex, a value closer to tetrahedral. Figures 2 and 3 illustrate the coordination environment of the Cd<sup>2+</sup> ions. The length of the Ag<sup>+</sup>-O<sup>2-</sup> bonds have increased from 2.25 Å in dehydrated Ag<sub>12</sub>-A compared to 2.49(1) Å in ethylene sorption complexes.<sup>3</sup> The O(3)-Ag<sup>+</sup>-O(3) bond angles have decreased from a nearly planar value, 119.6(4)° in dehydrated Ag<sub>12</sub>-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<sub>4</sub>Na<sub>4</sub>-A<sup>16</sup> 1.21(11) Å and that of Ag<sub>12</sub>-A,<sup>5</sup> 1.19(12) Å 1.19(12) Å. For comparison, the C-C bond length in ethylene gas is 1.334 Å.<sup>17</sup>

The bonding between the Cd<sup>2+</sup> ion at Cd(1) and ethylene can be described in terms of two components according to the Chatt Dewar model.<sup>18</sup> A  $\sigma$  component arises from the overlap of a filled ethylene orbital and a vacant Cd<sup>2+</sup> 5s orbital and a  $\pi$  component occurs by the overlap of the filled 4d orbitals of Cd<sup>2+</sup> with the vacant antibonding  $\pi^*$  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 4d electrons to the  $\pi^*$  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.<sup>19</sup> This suggests that the filled 4d orbitals of Cd<sup>2+</sup> ion do not reach sufficiently far out in space to effectively, whereas types of silver do. The Cd<sup>2+</sup> ion can not form an effective back bonding with ethylene because its d orbital are probably too contracted. The Ag<sup>+</sup>-C distance, 2.54 Å in Ag<sup>+</sup>-ethylene sorption complexes of Ag<sup>+</sup>-A is shorter than the present Cd<sup>2+</sup>-C distance, 2.67(6) Å.<sup>5</sup> Therefore Cd<sup>2+</sup>-C<sub>2</sub>H<sub>4</sub> complexes in zeolite A have a little weaker interaction than Ag<sup>+</sup>-C<sub>2</sub>H<sub>4</sub> complexes.

Carter *et al.*<sup>3</sup> 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<sup>+</sup> or Cd<sup>2+</sup>. The Cd(1)-C bond length, herein reported as 2.67(6) Å indicates that ethylene is moderately interacted with the Cd<sup>2+</sup> 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<sup>2+</sup> 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.

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