

카드뮴 이온으로 완전히 치환된 제올라이트 A를 진공 탈수한 후 브롬 증기로 흡착한 두개의 결정구조

고 광 락 · 장 세 복 · 박 종 열 · 김 덕 수⁺ · 김 양

부산대학교 화학과 · ⁺제주대학교 화학과
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Two Crystal Structures of Bromine Sorption Complexes of Vacuum Dehydrated Fully Cd(II) - Exchanged Zeolite A

Kwang Nak Koh, Se Bok Jang, Jong Yul Park, Duk Soo Kim⁺ and Yang Kim

Dept. of Chemistry, Pusan National University, Pusan 609 - 735

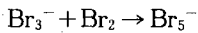
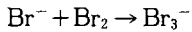
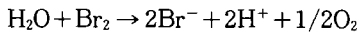
⁺Dept. of Chemistry, Cheju National University, Cheju 690 - 756

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요 약

Cd²⁺ 이온으로 이온 교환된 제올라이트 A를 진공 탈수한 후 브롬을 흡착한 두개의 결정구조를 단결정 X-선 회절법으로 해석하였다. 이들 결정은 21°C에서 입방공간군 Pm3m을 사용하여 해석하고 정산(精算)하였다. 두 결정은 Cd(NO₃)₂와 Cd(OOCCH₃)₂의 몰분율이 1 : 1이고 전체농도가 0.05M 되도록 만든 혼합용액을 이용하여 흐름법으로 이온교환하여 제조하였다. 첫번째 결정은 450°C에서 2 × 10⁻⁶ Torr의 진공하에서 2일간 탈수하였고, 두번째 결정은 650°C에서 2 × 10⁻⁶ Torr의 진공하에서 2일간 탈수하였다. 두 결정을 24°C에서 약 160Torr의 브롬증기로 반응시켰다. Full-matrix 최소자승법 정산에서 첫번째 결정(a=12.250(1) Å)과 두번째 결정(a=12.204(2) Å)의 마지막 오차인자는 I>3σ(I)인 212개의 독립반사

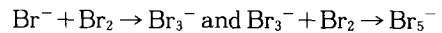
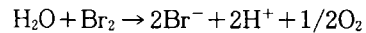
를 사용하여 R₁=0.075, R₂=0.079이며 128개의 독립반사를 사용하여 R₁=0.089, R₂=0.078까지 각각 정산하였다. 두 결정에서 단위세포당 6개의 Cd²⁺ 이온은 6-링 산소와 결합하면서 결정학적으로 서로 다른 2개의 3회 회전축상에 위치하고 있었다. 4.5개의 Cd²⁺ 이온은 Br₅⁻ 혹은 Br₃⁻의 이온과 착물을 형성하기 위해서 O(3)의 (111)평면에서 큰 동공쪽으로 약 0.441 Å 들어가 있었다. 나머지 1.5개의 Cd²⁺ 이온은 O(3)의 (111)평면에서 Sodalite 동공 깊숙히 약 0.678 Å 들어간 자리에 위치하였다. 단위세포당 약 1.5개의 Br₅⁻와 1.5개의 Br₃⁻ 이온이 흡착되었다. Br₅⁻ 이온결합은 2개의 Cd²⁺ 이온과 골조 산소이온과 착물을 이룸으로써 안정화되었다. Br₃⁻ 이온은 한 개의 Cd²⁺ 이온과 골조 산소이온과 결합하고 있었다. 생성된 Br₃⁻와 Br₅⁻는 브롬 분자가 잔류하는 물분자와 반응하여 다음과 같이 생성할 수 있다.



Abstract

Two crystal structures of bromine sorption complexes of vacuum dehydrated Cd(II)-exchanged zeolite A have been determined by single-crystal x-ray diffraction techniques in the cubic space group Pm3m at 21(1)°C. Both crystals were ion exchanged in flowing streams of exchange solution in which mole ratio of Cd(NO₃)₂ and Cd(OOCCH₃)₂ was 1 : 1 with a total concentration of 0.05 M. First crystal was dehydrated at 450°C and 2 × 10⁻⁶ Torr for two days. Second crystal was dehydrated at 650°C and 2 × 10⁻⁶ Torr for two days. Both crystals were then treated with 160 Torr for two days. Second crystal was dehydrated at 650°C and 2 × 10⁻⁶ Torr for two days. Both crystals were then treated with 160 Torr of zeolitically dried bromine vapor at 24°C. Full-matrix least-squares refinements of the first crystal (a = 12.250(1) Å) and the second crystal (a = 12.204(2) Å) have converged to final error indices, R₁ = 0.075 and R₂ = 0.079 with 212 reflections, and R₁ = 0.089 and R₂ = 0.078 with 128 reflections, respectively, for which I > 3σ(I). Crystallographic analyses of both crystals show that six Cd²⁺ ions are located on two different threefold axes of unit cell associated with 6-ring oxygens. Each 4.5 Cd²⁺ ion is recessed ca. 0.441 Å into the large cavity to complex either with Br₅⁻ or with Br₃⁻ from the (111) plane of O(3), whereas each 1.5 Cd²⁺ ions recessed ca. 0.678 Å into the sodalite unit. Approximately 1.5 Br₅⁻ and 1.5 Br₃⁻ ions are sorbed per unit cell. Each Br₅⁻ ion interacts and stabilized by complexing with two Cd²⁺ ions and framework oxide ions, while each Br₃⁻ ion interacts with one Cd²⁺ ion and framework oxide ions. Because of residual water molecules,

the following reactions may be occurred inside of zeolite cavity :



INTRODUCTION

The crystal structures of a bromine sorption complex of Na₁₂-A⁽¹⁾ and of a iodine sorption complex of Ca₄Na₄-A^(2,3) have been reported. About six bromine molecules per unit cell were sorbed into the bromine sorption complex of Na₁₂-A⁽¹⁾. However, these bromine molecules appeared to interact neither with the anionic framework nor with Na⁺ ions. On the other hand, in the crystal structure of an iodine sorption complex of Ca₄Na₄-A^(2,3), the 5.65 diiodine molecules sorbed per unit cell formed charge-transfer complexes with framework 8-ring oxygens (O-I-I = 178°)^(4,5).

Up to the now, several structures of halogen sorption complexes of Ag⁺,⁽⁶⁾ Eu(II)-,⁽⁷⁾ and Co(II)-⁽⁸⁻¹⁰⁾ exchanged zeolite A have been determined, respectively. In the structure of chlorine sorption complexes of vacuum-dehydrated Eu(II)-exchanged zeolite A, dichlorine has oxidized Eu(II) to Eu(IV)⁽⁷⁾. Chlorine gas also oxidizes hexasilver to AgCl as observed in the structure of a chlorine sorption complex of dehydrated fully Ag⁺-exchanged zeolite A.⁽⁶⁾ An additional six dichlorine molecules per unit cell are sorbed which form charge-transfer complexes with framework oxide ions (O-Cl-Cl = 166(2)°). In the crystal structure of a Cl₂ sorption complex of Co₄Na₄-A,⁽⁸⁾ four chlorine molecules act as ligands to coordinate, each to one Co(II) ion, in a bent manner. Dehydrated Co_{3.5}Na₅-A sorbs 2.5 molecules and 5.0 diiodine molecules per unit cell (vapor pressure of I₂ is 8.3 and 14.3 torr, respectively)⁽⁹⁾. Recently, the crystal structure of bromine sorption complexes of partially cobalt(II)-exchanged zeolite A have

been determined¹⁰). In this structure, 3.5 tribromide ions are found, indicating that Co(II) has been oxidized to Co(III). The atom at one end of each is involved in a linear charge-transfer complex with a framework oxygen and in a much weaker interaction with the opposite end atom of an adjacent tribromide ion.

This work was undertaken to further investigate the sorption properties of zeolite A and to determine the positions of the sorbed bromine molecules. The resulting structure, shows Br_5^- ions, indicating that the mechanism of sorption of Br_2 by $\text{Cd}_6\text{-A}$ is different from that of others inside zeolite A.

EXPERIMENTAL SECTION

Crystals of zeolite 4A were prepared by a modification of Charnell's method¹¹). Each of two single crystals 0.08mm on an edge was selected. One crystal was lodged in a finely drawn Pyrex glass capillary and the other in a quartz capillary. An exchange solution of $\text{Cd}(\text{NO}_3)_2$ in the mole fraction of 1 : 1 with a total concentration of 0.05 M was allowed to flow past each crystal at a velocity of approximately 1.0 cm/sec for 3 days. Each crystal was washed for 1 hr with distilled water at 80°C and 2×10^{-6} Torr for 48 hours and the second crystal lodged in a quartz capillary was dehydrated at 650°C and 2×10^{-6} Torr for 48 hours. After cooling to room temperature, the crystals, still under vacuum were sealed in its capillary by torch. Both crystals were colorless. To prepare the bromine complex, each crystal was treated with 160 Torr of zeolitically dried bromine vapor at 24°C¹²). The colorless dehydrated crystals immediately became dark red. After about 1 hr, each crystal, still in its bromine atmosphere, was sealed in its capillary by torch.

The space group $\text{Pm}\bar{3}\text{m}$ (no systematic absence) was used^{13,14}) throughout this work for reasons dis-

cussed previously. Preliminary crystallographic experiments and subsequent data collection were performed with an automated four-circle Enraf Nonius CAD4 diffractometer equipped with a graphite monochromator and a PDP micro 11/73 computer. Molybdenum radiation was used for all experiments ($K\alpha_1, \lambda = 0.70930 \text{ \AA}$; $K\alpha_2, \lambda = 0.71359 \text{ \AA}$). In each case, the cell constant, $a = 12.250(1) \text{ \AA}$ for the first crystal and $a = 12.204(2) \text{ \AA}$ for the second crystal, was determined by a least-squares treatment of 25 intense reflections for which $19^\circ < 2\theta < 24^\circ$ at 21(1)°C.

For both crystals, reflections from two intensity-equivalent regions of reciprocal space ($hkl, h \leq k \leq l$ and $lkh, l < k < h$) were examined. The intensities were measured using the $\omega - 2\theta$ scan technique over scan width of $(0.80 + 0.344 \tan\theta)$ in ω . The data were collected using variable scan speeds; the maximum final scan time was 5 minutes per reflection. Most reflections were observed at the slow scan speeds, ranging between 0.25° and 0.31° in ω /min. The intensities of three reflections in diverse regions of reciprocal space were recorded every 3 hours to monitor crystal and instrument 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 collected.

The raw data from each region were corrected for Lorentz and polarization effects; the reduced intensities were merged and the resultant estimated standard deviations were assigned to each average reflection by the computer programs PAINT and WEIGHT¹⁵).

An absorption correction ($\rho_{\text{cal}} = 2.76 \text{ gcm}^{-3}$, $F(000) = 1410$, and μR for each crystal ca. 0.35) was judged to be negligible and was not applied¹⁶). Only those reflections in each merged data set for which the net count exceeded three times its corre-

sponding esd's were used in structure solution and refinement. These amounted to 212 of the 874 reflections examined for the first crystal and 128 of the 862 reflections for the second crystal.

STRUCTURE DETERMINATION

Full-matrix least-squares refinement was initiated using the atomic parameters of the framework atoms[(Si, Al), O(1), O(2), and O(3)] and a Cd²⁺ from the ethylene complex of dehydrated fully Cd

(II)-exchanged zeolite A¹⁷⁾. Anisotropic refinement of the framework atoms and Cd²⁺ at Cd(1) and Cd(2) converged to $R_1 = \sum(F_0 - F_C) / \sum F_0 = 0.490$ and $R_2 = (\sum W(F_0 - F_C)^2 / \sum W F_0^2)^{1/2} = 0.537$ for the first crystal and $R_1 = 0.395$ and $R_2 = 0.451$, for the second crystal. The Cd²⁺ ions at Cd(1) and Cd(2) are associated with 6-rings and lie on two nonequivalent 3-fold axes. The occupancy numbers of Cd²⁺ ions per unit cell were refined to Cd(1) = 4.4(1) and Cd(2) = 1.6(1) (see Table 1). these were fixed at Cd(1) = 4.5 and Cd(2) = 1.5 be-

Table 1. ^a Positional, Thermal, and Occupancy Parameters
Crystal 1. Bromine Sorption Complex of the Fully Cd(II)-Exchanged Zeolite A Dehydrated at 450 °C

Atom	wyc. pos.	x	y	z	^b β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy
(Si,Al)	24(k)	0	1825(5)	3684(4)	28(3)	18(3)	17(3)	0	0	3(7)	1.0 ^c
O(1)	12(h)	0	2000(20)	5000	50(20)	70(20)	20(10)	0	0	0	1.0
O(2)	12(i)	0	2960(10)	2960(10)	50(20)	32(8)	32(8)	0	0	70(30)	1.0
O(3)	24(m)	1134(7)	1134(7)	3290(10)	29(6)	29(6)	50(10)	0(20)	-10(10)	-10(10)	1.0
Cd(1)	8(g)	2084(3)	2084(3)	2084(3)	53(2)	53(2)	53(2)	66(5)	66(5)	66(5)	4.5/8
Cd(2)	8(g)	1556(7)	1556(7)	1556(7)	18(4)	18(4)	18(4)	20(10)	20(10)	20(10)	1.5/8
Br(1)	24(1)	888(10)	4750(20)	5000	90(10)	80(20)	80(20)	-70(30)	0	0	1/8
Br(2)	24(1)	2120(40)	3780(30)	5000	810(50)	1020(60)	420(90)	-1780(60)	0	0	1/8
Br(3)	24(m)	3150(10)	3150(10)	3690(10)	200(10)	200(10)	120(20)	-220(30)	40(20)	40(20)	4.5/24
Br(4)	12(j)	3360(30)	3360(30)	5000	120(30)	120(30)	280(80)	0(80)	0	0	3/24

Crystal 2. Bromine Sorption Complex of the Fully Cd(II)-Exchanged Zeolite A Dehydrated at 650 °C

Atom	wyc. pos.	x	y	z	^b β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy
(Si, Al)	24(k)	0	1821(8)	3682(7)	8(5)	9(5)	55(7)	0	0	0(10)	1.0 ^c
O(1)	12(h)	0	1820(30)	5000	130(40)	50(30)	80(30)	0	0	0	1.0
O(2)	12(i)	0	2930(20)	2930(20)	40(30)	80(20)	80(20)	0	0	-40(60)	1.0
O(3)	24(m)	1140(10)	1140(10)	3340(20)	32(9)	32(9)	60(20)	90(20)	60(20)	60(20)	1.0
Cd(1)	8(g)	2057(5)	2057(5)	2057(5)	62(3)	62(3)	62(3)	70(8)	70(8)	70(8)	4.5/8
Cd(2)	8(g)	1530(10)	1530(10)	1530(10)	3(6)	3(6)	3(6)	30(10)	30(10)	30(10)	1.5/8
Br(1)	24(1)	1020(20)	4640(20)	5000	190(40)	30(30)	30(20)	-60(40)	0	0	1/8
Br(2)	24(1)	2390(40)	3750(50)	5000	120(40)	700(100)	160(70)	-490(90)	0	0	1/8
Br(3)	24(m)	3238(20)	3238(20)	3550(30)	360(20)	360(20)	220(40)	-470(80)	-40(40)	-40(40)	4.5/24
Br(4)	12(j)	3030(40)	3030(40)	5000	170(50)	170(50)	800(200)	-300(100)	0	0	3/24

^a 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. ^b The anisotropic temperature factor = $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. ^c Occupancy for (Si) = 1/2; Occupancy for (Al) = 1/2.

cause the cationic charge should not be exceeded + 12 per Pm3m unit cell. The similar positions and occupancies were found in previous structure^{7, 18)}.

From the initial difference Fourier function, Br(1) and Br(2) were readily located and refined. The bromine species at Br(1) are associated with 8-ring oxygens and close to Br(2). Furthermore the occupancy number of Br(2) was almost

equal to that of Br(2). Also, the distance between Br(1) and Br(2) represents the dibromine molecules. Therefore the occupancy number of Br(2) was constrained to that of Br(1). The occupancy number of Br(1) was refined at 2.99(10). This number was fixed at 3.0 because the zeolite A structure contains three 8-rings per unit cell and each bromine species of Br(1)-Br(2) appeared to be associated with one 8-ring. Inclusion of Br

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

Atom	Crystal 1	Crystal 2
(Si, Al) - O(1)	1.627(6)	1.609(8)
(Si, Al) - O(2)	1.65(1)	1.64(2)
(Si, Al) - O(3)	1.697(7)	1.67(1)
Cd(1) - O(3)	2.21(1)	2.22(2)
Cd(2) - O(1)	2.25(1)	2.31(2)
Br(1) - O(1)	3.54(3)	3.66(4)
Br(1) - O(2)	3.50(2)	3.51(2)
Br(1) - Br(2)	2.25(5)	2.59(6)
Br(2) - Br(3)	2.60(2)	2.37(3)
Br(3) - Br(4)	2.33(1)	2.21(3)
Cd(1) - Br(3)	2.69(1)	2.80(3)
O(1) - (Si,Al) - O(2)	115.1(9)	124(2)
O(1) - (Si,Al) - O(3)	110.2(6)	105(2)
O(2) - (Si,Al) - O(3)	105.6(4)	105.7(7)
O(3) - (Si,Al) - O(3)	109.9(5)	112.3(7)
(Si,Al) - O(1) - (Si,Al)	165(2)	181(3)
(Si,Al) - O(2) - (Si,Al)	155.0(7)	158(1)
(Si,Al) - O(3) - (Si,Al)	137.5(7)	140(2)
O(3) - Cd(1) - O(3)	115.2(3)	117.0(4)
O(3) - Cd(2) - O(3)	112.5(3)	110.6(5)
O(3) - Cd(1) - Br(3)	108.4(3)	102.9(5)
Cd(1) - Br(3) - Br(2)	103(2)	101(1)
Br(1) - Br(2) - Br(3)	104(2)	103(1)
O(1) - Br(1) - Br(2)	158(1)	159(1)
Cd(1) - Br(3) - Br(4)	113.7(7)	117(1)
Br(3) - Br(4) - Br(3)	154(2)	144(2)
Br(2) - Br(3) - Br(4)	117(1)	127(1)
O(2) - Br(1) - Br(2)	143(1)	148(1)

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

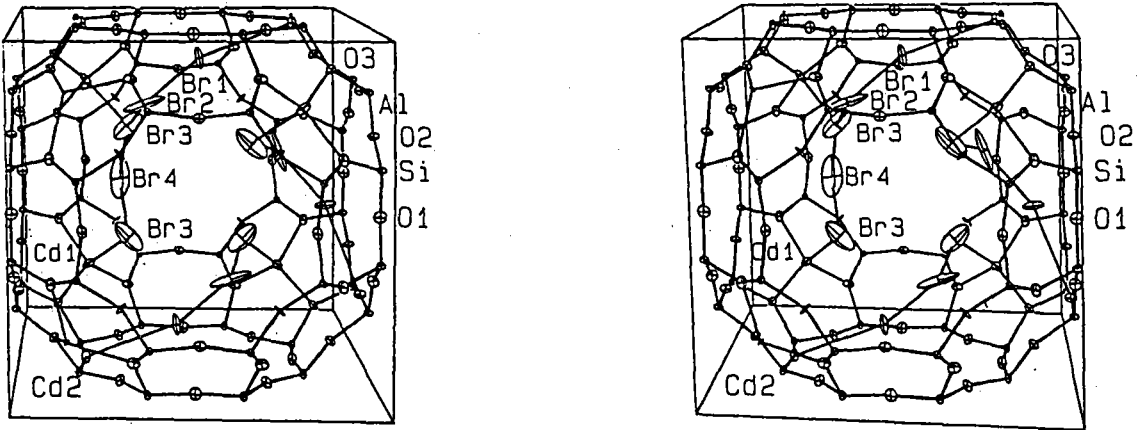


Figure 1. The stereoview of large cavity of a bromine sorption complex of dehydrated Cd_6-A . About 50% of the unit cell may have this arrangement. The remaining 50% may contain 5 Cd^{2+} ions at Cd(1), 1 Cd^{2+} ions at Cd(2), one Br_3^- and two Br_5^- . Ellipsoids of 20% probability are used.

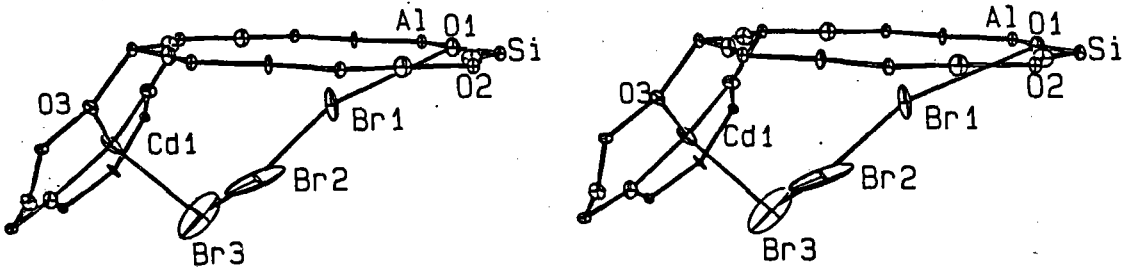


Figure 2. A stereoview of one corner of the large cavity showing the Br_3^- ion coordinated to Cd^{2+} ion at Cd (1). Ellipsoids of 20% probability are used.

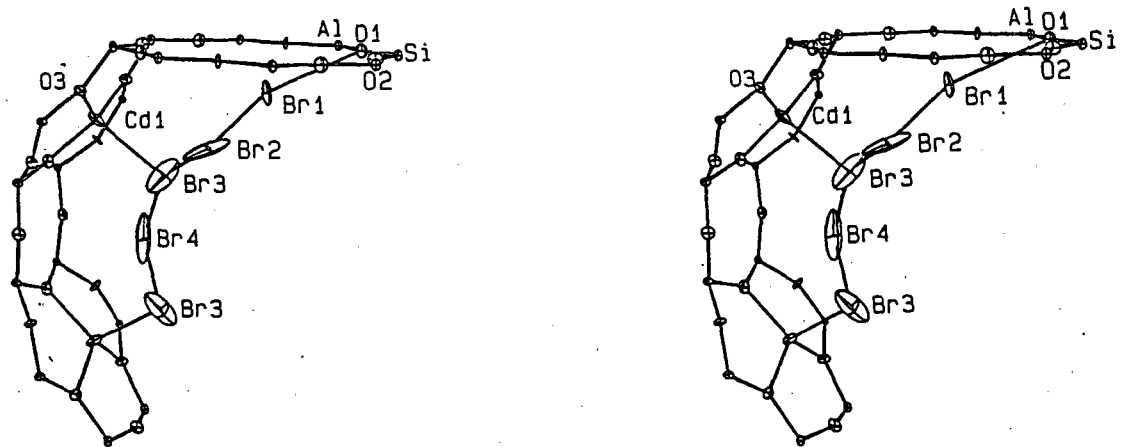


Figure 3. A stereoview of one corner of the large cavity showing the Br_5^- . Ellipsoids of 20% probability are shown.

(1) and Br(2) lowered the error indexes to $R_1=0.217$ and $R_2=0.361$ for the first crystal and $R_1=0.213$ and $R_2=0.304$ for the second crystal(see Table 1). From a subsequent difference Fourier map, Br species at Br(3) was located. The occupancy number of Br(3) was refined to 4.9(1). The occupancies at Br(3) and Cd(1), and their interatomic distances indicated that these are associated with each other. Therefore the occupancy of Br(3) was fixed at 4.5, the same number as Cd(1) (see Table 1). Inclusion Br(3) in a least-squares refinement lowered to $R_1=0.111$ and $R_2=0.111$ for first crystal, and $R_1=0.107$ and $R_2=0.103$ for the second crystal.

Successive difference Fourier map revealed the bromine position Br(4) (0.3320, 0.3320, 0.5) with a peak heights of $3.4(1) e\text{\AA}^{-3}$ and $2.89(3) e\text{\AA}^{-3}$, respectively. The occupancy number of Br(4) was refined to ca. 1.4(1). This Br(4) is close to Br(3). Furthermore the occupancies of Br(i), $i=1, 2, 3$, and 4(Table 1), and their interatomic distances (Table 2) indicated that $1.5 Br_3^-$ and $1.5 Br_5^-$ species have formed per unit cell(see Figure 1, 2, and 3). Therefore the occupancy of Br(4) was fixed at 1.5 per unit cell. The structures were refined to give the final error indexes $R_1=0.075$ and $R_2=0.079$ for the first crystal, and $R_1=0.089$ and $R_2=0.078$ for the second crystal. The final difference Fourier function was featureless except for one peak at (0, 0, 0) with peak height $4.4(20) e\text{\AA}^{-3}$ for the first crystal and one at (0, 0, 0) with peak

height $3.2(21) e\text{\AA}^{-3}$ for the second crystal.

Atomic scattering factors for Cd^{2+} , O^- , Br^0 and (Si, Al) $^{1.75+}$ were used^{19,20}. The function describing (Si, Al) $^{1.75+}$ is the mean of the Si^0 , Si^{4+} , Al^0 and Al^{3+} function. All scattering factors were modified to account for anomalous dispersion correction^{21,22}. Final positional, thermal and occupancy parameters are presented in Table 1. Bond lengths and angles are given in Table 2.

DISCUSSION

In the crystal structures of a bromine sorption complex of dehydrated fully Cd(II) exchanged zeolite A, all six Cd^{2+} ions are found on two distinguished three axes of unit cell. About 4.5 ions at Cd (II) extended ca. 0.44\AA into the large cavity from the (111) plane at O(3) and are coordinated to three O(3) oxygens at ca. 2.22\AA . These Cd^{2+} ions are also complexed with bromine species at Br (3). About 1.5 Cd^{2+} ions are recessed ca. 0.64\AA into the sodalite unit from the O(3)plane of the 6 ring. Each of these Cd^{2+} ions is coordinated to three O(3) framework oxygens at 2.28\AA .

The number of bromine atom or ion at Br(i), $i=1-4$, are 3.0, 3.0, 4.5 and 1.5. These bromine species are all located inside the large cavity. They may be placed within their equipoints of partial occupancy. They are rather close to each other : Br (1) - Br(2) = ca. 2.47\AA , Br(2) - Br(3) = ca. 2.48\AA , and Br(3) - Br(4) = ca. 2.27\AA . Their occupancies and interatomic distances suggest that 1.5

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

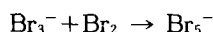
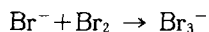
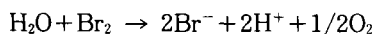
Atom	Crystal 1	Crystal 2
O(2)	0.26(1)	0.17(1)
Cd(1)	0.49(1)	0.39(1)
Cd(2)	-0.63(1)	-0.72(1)
Br(3)	3.13(1)	3.90(1)

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

$\text{Br}_5^-((\text{Br}(1) - \text{Br}(2) - \text{Br}(3) - \text{Br}(4) - \text{Br}(3))^-)$ and $1.5 \text{ Br}_3^-((\text{Br}(1) - \text{Br}(2) - \text{Br}(3))^-)$ are formed per unit cell (see Figure 1 to 3).

The fractional occupancies observed at Cd(1), Cd(2), and Br(i), $i=1-4$, indicate the existence of 2 types of unit cell. About 50% of unit cell may have 4 Cd^{2+} ions at Cd(1), 2 Cd^{2+} ion at Cd(2), 2 Br_3^- and 1 Br_5^- (see Figure 1). The remaining 50% would have 5 Cd^{2+} ions at Cd(1), 1 Cd^{2+} ions at Cd(2), 1 Br_3^- and 2 Br_5^- .

The existence of Br_3^- and Br_5^- inside the large cavity indicate that the following reaction may be occurred with the residual water molecules in vacuum dehydrated Cd(II) exchanged zeolite A^{23,24}:



These Br_5^- and Br_3^- ions are asymmetric in bond length (see Table 2) and bent ($\text{Br}(1) - \text{Br}(2) - \text{Br}(3) = 103.5^\circ$, $\text{Br}(2) - \text{Br}(3) - \text{Br}(4) = 122^\circ$, and $\text{Br}(3) - \text{Br}(4) - \text{Br}(3) = 149^\circ$) (see Table 2).

Br_5^- and Br_3^- ions have previously been found to be sometimes symmetric and sometimes asymmetric^{25,26}. Also the overall length of I_5^- and I_3^- ions, which have been studied in most detail, is approximately 0.5 Å more than twice the single bond length²⁵. In the crystal structure of cesium tribromide, the following geometry is reported: $\text{Br}(1) - \text{Br}(2) = 2.698(6)$ Å, $\text{Br}(2) - \text{Br}(3) = 2.440(6)$ Å, and $\text{Br}(1) - \text{Br}(2) - \text{Br}(3) = 177.5^\circ$ ²⁷. For comparison, the Br-Br distance in free dibromine is 2.29 Å²⁸. Each Br_5^- ion interacts and stabilizes by complexing with two Cd^{2+} ions and framework oxide ions, O(1) and O(2). The Br(1) to O(1) and Br(1) to O(2) distances (3.60 Å and 3.50 Å, respectively) are longer than the sum of van der Waals radii of Br and O, 3.35 Å²⁹. On the other hands, each Br_3^- ion interacts and stabilizes by complexing with one Cd^{2+} ion and framework oxide ions. The bonding distance between Cd^{2+}

ions at Cd(1) and Br species at Br(3) is ca. 2.75 Å. This distance is much shorter than the sum of the van der Waals radius of Br and the ionic radius of Cd^{2+} (2.93 Å)³⁰, and also shorter than the sum of the ionic radii of Cd^{2+} and Br^- (2.92 Å)³⁰. There this bonding characters must be somewhat covalent.

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Supplementary Table 1.

Values of $10 \times F_{\text{obs}}$ and $10 \times F_{\text{calc}}$

H	K	L	F_{obs}	F_{calc}	SiaF	H	K	L	F_{obs}	F_{calc}	SiaF
0	0	1	506	619	8	0	3	14	457	501	36
0	0	2	1576	1500	43	0	3	17	405	442	52
0	0	3	359	351	17	0	4	4	1005	967	10
0	0	4	222	179	27	0	4	5	890	899	28
0	0	5	1119	1111	10	0	4	6	644	644	14
0	0	6	2971	3156	55	0	4	7	1310	1381	12
0	0	7	999	1037	18	0	4	10	348	299	34
0	0	8	519	513	18	0	4	12	624	591	26
0	0	9	781	780	15	0	4	14	352	309	45
0	0	10	1517	1534	41	0	5	5	2982	2939	8
0	0	11	941	932	16	0	5	6	786	726	13
0	0	14	561	524	30	0	5	7	850	874	14
0	0	16	510	391	38	0	5	8	337	337	46
0	1	1	208	382	19	0	5	10	548	608	28
0	1	2	532	876	20	0	5	11	660	711	23
0	1	3	890	831	14	0	5	12	320	355	42
0	1	4	654	623	11	0	6	6	1301	1288	11
0	1	5	398	494	29	0	6	8	335	201	33
0	1	6	501	483	15	0	6	9	444	448	27
0	1	7	420	431	19	0	6	11	914	885	19
0	1	9	340	362	33	0	7	7	933	901	15
0	1	12	357	324	36	0	7	9	911	947	19
0	2	2	1063	923	20	0	7	10	781	864	20
0	2	3	248	265	25	0	9	9	501	534	31
0	2	4	587	604	26	0	9	11	343	366	45
0	2	5	1302	1386	15	0	9	12	613	570	29
0	2	9	853	921	14	0	10	10	782	810	24
0	2	10	364	374	31	0	10	12	429	524	43
0	2	12	366	331	53	0	11	11	917	915	24
0	2	13	317	250	43	0	11	16	526	467	50
0	2	15	355	230	46	1	1	1	324	558	17
0	3	3	1730	1552	33	1	1	2	801	745	20
0	3	4	333	373	36	1	1	3	1479	1444	20
0	3	5	1000	935	11	1	1	4	1052	1012	19
0	3	7	532	532	17	1	1	5	382	346	19
0	3	11	501	411	42	1	1	7	322	348	24

H	K	L	F _{obs}	F _{calc}	SiaF
1	1	10	584	609	21
1	2	2	1219	1105	12
1	2	3	1351	1216	7
1	2	4	536	547	13
1	2	6	291	252	24
1	2	7	341	326	24
1	2	8	439	478	26
1	3	3	390	329	16
1	3	5	304	345	23
1	3	6	728	711	13
1	3	7	681	674	15
1	3	8	382	379	25
1	3	9	512	505	21
1	3	17	377	265	55
1	4	4	752	728	11
1	4	5	437	504	18
1	4	6	519	575	27
1	4	7	387	273	37
1	4	8	563	575	18
1	4	11	358	352	35
1	4	12	324	417	42
1	4	14	334	243	49
1	5	7	763	817	32
1	5	8	350	315	29
1	5	12	315	231	43
1	6	7	274	267	34
1	6	8	505	494	24
1	6	9	364	312	32
1	7	7	330	307	33
1	7	8	399	381	29
1	7	10	403	438	33
1	9	9	456	463	31
2	2	2	607	648	11
2	2	3	1879	1898	6
2	2	4	909	881	16
2	2	5	1090	1119	9
2	2	6	214	243	32
2	2	7	829	833	13

H	K	L	F _{obs}	F _{calc}	SiaF
2	2	8	543	539	19
2	2	9	716	688	22
2	2	10	479	429	26
2	2	11	306	349	39
2	2	15	391	355	44
2	2	16	346	299	51
2	3	3	1736	1705	7
2	3	4	312	321	21
2	3	5	795	738	11
2	3	8	1102	1138	12
2	3	9	342	315	31
2	3	11	364	353	34
2	3	15	342	268	49
2	4	4	435	420	17
2	4	5	846	867	11
2	4	7	821	792	14
2	4	8	328	241	28
2	4	12	338	335	39
2	5	7	663	645	17
2	5	8	502	531	32
2	5	9	382	294	31
2	5	10	553	526	24
2	5	11	289	245	42
2	5	12	324	336	42
2	5	14	342	339	49
2	6	6	529	601	22
2	6	7	377	352	27
2	7	9	821	792	21
2	8	8	882	951	24
2	8	13	373	336	44
2	9	10	337	255	43
2	9	12	525	542	35
3	3	3	1292	1269	17
3	3	4	284	231	24
3	3	5	361	302	20
3	3	6	585	592	17
3	3	8	1688	1795	39
3	3	9	493	549	24

H	K	L	F _{obs}	F _{calc}	SiaF
3	3	16	410	338	47
3	4	4	415	439	18
3	4	6	796	735	13
3	4	7	1004	963	13
3	4	12	563	535	27
3	5	5	851	852	27
3	5	7	453	427	22
3	5	9	452	443	27
3	5	12	474	480	31
3	6	10	291	292	41
3	7	9	714	771	20
3	7	10	795	803	20
3	7	15	372	340	55
3	8	8	1147	1150	15
3	8	9	288	266	44
3	8	13	624	662	31
3	8	14	496	531	41
3	9	9	354	342	39
3	9	12	455	435	39
3	9	14	387	277	52
4	4	5	528	501	17
4	4	6	444	384	21
4	4	7	266	261	39
4	4	8	361	378	30
4	4	9	637	602	20
4	4	11	554	524	50
4	4	13	342	353	46
4	4	14	392	417	45
4	5	7	831	834	15
4	5	9	413	381	29
4	5	11	300	350	44
4	5	12	481	458	33
4	6	6	429	423	24
4	6	7	503	516	23
4	7	7	638	671	21
4	7	8	374	336	32
4	9	9	298	184	45
4	9	11	322	343	49

H	K	L	F _{obs}	F _{calc}	SiaF
5	5	5	1104	1102	12
5	5	6	651	762	19
5	5	7	1159	1188	16
5	5	8	365	336	32
5	5	9	416	375	47
5	5	10	590	557	25
5	5	11	441	480	33
5	6	6	856	856	16
5	6	9	366	301	35
5	6	11	530	516	31
5	6	18	450	103	56
5	7	9	613	627	24
5	7	10	649	621	24
5	7	15	381	341	56
5	8	8	356	374	35
5	8	11	387	223	42
5	11	11	645	669	32
6	6	6	663	604	37
6	6	11	395	319	39
6	7	10	394	398	39
6	8	10	315	116	47
6	11	11	479	395	43
7	7	11	436	391	39
7	8	9	366	210	41
8	8	8	1082	1083	19
8	8	13	402	378	53

Observed and calculated structure factors for a bromine sorption complex of dehydrated fully Cd²⁺-exchanged zeolite A at 450 °C.

Supplementary Table 2.

Values of $10 \times F_{obs}$ and $10 \times F_{calc}$

H	K	L	F_{obs}	F_{calc}	SiaF
0	0	1	640	659	19
0	0	2	1392	1566	55
0	0	3	570	598	21
0	0	5	1182	1222	36
0	0	6	3032	3168	143
0	0	7	631	622	32
0	0	8	569	606	30
0	0	9	687	687	30
0	0	10	1363	1345	97
0	0	11	1015	997	27
0	0	14	468	402	57
0	1	1	267	272	28
0	1	2	460	683	22
0	1	3	782	762	17
0	1	4	839	846	17
0	1	6	579	624	62
0	1	9	420	329	42
0	2	2	623	607	22
0	2	4	513	556	24
0	2	5	1050	1274	47
0	2	9	682	858	63
0	3	3	1697	1674	11
0	3	5	926	881	26
0	4	4	1025	1015	19
0	4	5	842	808	19
0	4	6	630	655	25
0	4	7	1172	1221	60
0	4	12	588	529	46
0	5	5	2770	2814	23
0	5	6	928	908	21
0	5	7	805	782	26
0	5	9	406	230	52
0	5	10	539	689	42
0	5	11	762	733	51
0	6	6	1349	1362	18
0	6	8	374	247	53
0	6	9	460	441	48
0	6	11	852	859	33

H	K	L	F_{obs}	F_{calc}	SiaF
0	7	7	802	721	30
0	7	9	843	906	30
0	7	10	720	865	51
0	10	10	769	823	41
0	11	11	876	920	41
1	1	2	821	842	18
1	1	3	1301	1313	45
1	1	4	961	732	53
1	1	5	414	324	52
1	1	10	624	602	37
1	2	2	1351	1245	11
1	2	3	1411	1196	38
1	2	4	559	494	22
1	3	3	388	244	29
1	3	6	620	653	25
1	3	7	613	581	33
1	3	9	581	615	33
1	3	10	498	492	45
1	4	4	685	665	21
1	4	5	430	476	62
1	4	7	382	276	42
1	4	8	444	409	41
1	4	12	477	392	51
1	5	7	655	670	30
1	7	8	367	450	56
1	7	10	557	476	42
1	8	9	372	258	56
1	9	9	497	510	49
2	2	2	545	594	23
2	2	3	1816	1872	22
2	2	4	780	717	18
2	2	5	995	1222	49
2	2	7	602	617	27
2	2	8	605	464	52
2	2	9	686	603	31
2	3	3	1681	1087	11
2	3	5	651	642	22
2	3	8	1027	1068	43

H	K	L	F _{obs}	F _{calc}	SiaF
2	4	5	653	681	43
2	4	7	763	739	25
2	5	7	502	507	37
2	5	8	458	465	44
2	5	12	405	289	55
2	6	6	499	507	37
2	7	9	737	668	61
2	8	8	892	870	28
2	9	12	489	421	63
2	10	12	439	253	67
3	3	3	1300	1303	13
3	3	6	734	733	27
3	3	7	444	217	38
3	3	8	1594	1724	61
3	3	9	621	575	36
3	3	14	416	226	64
3	4	4	496	565	28
3	4	6	721	586	59
3	4	7	1051	1023	21
3	4	12	617	559	44
3	5	5	698	674	25
3	5	12	471	323	55
3	7	9	675	680	37
3	7	10	801	805	34
3	8	8	1127	1148	34
3	8	9	382	350	58
3	8	13	571	696	58
3	9	9	404	323	62
3	10	12	464	416	69
4	4	5	617	542	36
4	4	9	557	637	41
4	4	11	581	637	45
4	5	7	765	829	29
4	6	6	482	426	40
4	6	7	571	489	39
4	7	7	543	446	42
4	7	8	412	285	52
4	8	12	440	312	66

H	K	L	F _{obs}	F _{calc}	SiaF
5	5	5	1046	1057	22
5	5	6	666	795	32
5	5	7	955	961	36
5	5	10	531	693	80
5	6	6	830	747	74
5	7	9	537	460	47
5	7	10	630	544	53
5	11	11	513	592	68
6	6	6	841	838	29
6	6	9	388	385	58
6	6	13	454	264	65
6	7	10	438	478	61
7	7	9	485	322	53
8	8	8	1055	1049	33

Observed and calculated structure factors for a bromine sorption complex of dehydrated fully Cd²⁺-exchanged zeolite A at 650 °C.