

칼슘이온으로 완전히 치환한 제올라이트 A를 탈수한 후 브롬을 흡착한 결정구조

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The Crystal Structure of a Bromine Sorption Complex of Dehydrated Fully Ca^{2+} -Exchanged zeolite A

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요 약. 완전히 Ca^{2+} 이온으로 치환한 제올라이트 A를 탈수한 후 브롬을 흡착한 결정구조($a=12.211(2)$ Å)를 입방공간군 $Pm3m$ 을 써서 단결정 X-선 회절법으로 해석하였다. 결정은 360°C 에서 2×10^{-6} Torr하에서 2일간 진공 탈수한 후 24°C 에서 약 180 Torr의 브롬 기체로써 30분간 반응시켰다. 결과로 얻은 구조에서 6개의 Ca^{2+} 이온은 6-링 산소와 결합하면서 두개의 다른 3회 회전축상에 위치하고 있었고 단위 세포당 총 6분자의 브롬이 흡착되었다. 각 브롬 분자는 골격구조의 산소이온과 전하이동착물을 형성하였다(O-Br=3.12(7) Å, Br-Br=2.64(9) Å 및 O-Br-Br=178(2)°). Full-matrix 최소자승법 정밀화 계산에서 $I > 3\sigma(I)$ 인 103개의 독립반사를 써서 $R=0.104$ 까지 얻었다.

ABSTRACT. The crystal structure of a bromine sorption complex of dehydrated fully Ca^{2+} -exchanged zeolite A ($a=12.211(2)$ Å) has been determined by single-crystal X-ray diffraction techniques in the cubic space group, $Pm3m$ at $21(1)^\circ\text{C}$. The crystal was prepared by dehydration at 360°C and 2×10^{-6} Torr for 2 days, followed by exposure to about 180 Torr of bromine vapor at 24°C for 30 min. In the resulting structure, six Ca^{2+} ions are located on two different threefold axes associated with 6-ring oxygens. A total of six dibromine molecules are sorbed per unit cell. Each Br_2 molecule approaches a framework oxide ion axially, with O-Br=3.12(7) Å, Br-Br=2.64(9) Å and O-Br-Br=178(2)°, indicating a charge-transfer interaction. Full-matrix least-squares refinement converged to a conventional R index of 0.104 using the 103 independent reflections for which $I > 3\sigma(I)$.

Introduction

In the crystal structure of a bromine sorption complex of zeolite 4A ($\text{Na}_{12}\text{-A}$)¹², six dibromine molecules were sorbed per unit cell. They appeared to interact neither with the anionic framework nor with Na^+ ions. When Br_2 gas was sorbed onto a single crystal of vacuum-dehydrated $\text{Ag}_{12}\text{-A}^3$, 6 bromine molecules are sorbed per unit cell; 3.6 Br_2 molecules coordinate to draw 3.6 of

the 8 6-ring Ag^+ ions into large cavity, and 2.4 Br_2 molecules form charge transfer complexes with framework oxygens (O-Br-Br=174(4)°). In the crystal structure of a bromine sorption complex of dehydrated partially cobalt(II)-exchanged zeolite A⁴, a redox reaction has apparently occurred between Co(II) and Br_2 to yield Co(III) and Br_3^- ions. The 4 Na^+ and 4 Co^{3+} ions per unit cell occupy 6-ring sites on 3-fold axes. Four quite

asymmetric Br_3^- ions^{5,6}, each bridges between a Co^{3+} ion and an 8-ring framework oxygens ($(\text{Br}-\text{Br}-\text{Br})^- = 138^\circ$ and $\text{Br}-\text{Br}-\text{O} = 177^\circ$). The near linear $\text{Br}-\text{Br}-\text{O}$ angle is indicative of a charge transfer interaction. Two other bromine molecules similarly form charge transfer complexes with 8-ring oxygens⁴.

In the crystal structures of the iodine sorption complexes of $\text{Ca}_4\text{Na}_4\text{-A}^7$ and $\text{Ca}_6\text{-A}^8$, ca. six diiodine molecules sorbed per unit cell formed charge-transfer complexes with framework 8-ring oxygens. Neither iodine- Ca^{2+} nor iodine- Na^+ interaction was observed. In the crystal structures of iodine sorption complexes of $\text{Co}_{3.5}\text{Na}_5\text{-A}^9$, 2.5 diiodine molecules per unit cell were sorbed at 70°C within 30 minutes and 5 iodine molecules per unit cell at 80°C after 24 h. Again, each iodine molecule makes a close nearly linear approach ($\text{I}-\text{I}-\text{O} = 175^\circ$), indicative of charge-transfer complexation, to an 8-ring oxygen.

In the crystal structures of chlorine sorption complexes of Eu(II) -exchanged zeolite A^{10} and Ag^+ -exchanged zeolite A^{11} , chlorine gas is reported to have oxidized Eu(II) to Eu(IV) ¹⁰ and hexa-silver to AgCl^{11} . In the latter structure, an additional 6 dichlorine molecules are sorbed per unit cell; these form charge-transfer complexes with framework oxygens ($\text{O}-\text{Cl}-\text{Cl} = 166(2)^\circ$). When Cl_2 gas was sorbed onto a single crystal of vacuum-dehydrated $\text{Co}_4\text{Na}_4\text{-A}^{12}$, dichlorine molecules coordinated to Co(II) in a bent manner. The chlorine molecule is essentially basic with respect to the hard acid Co(II) , and the dichlorine bond is lengthened by a large amount, approximately 0.5\AA , upon complexation¹².

This work was undertaken to investigate bromine sorption by dehydrated $\text{Ca}_6\text{-A}$ and to determine the positions of sorbed bromine molecules.

Experimental Section

Crystals of zeolite 4A were prepared by a modification of Charnell's method¹³, including a second crystallization using seed crystals from the first synthesis. A single crystal 0.08 mm on an edge was lodged in a fine glass capillary. An exchange

solution of $0.04325\text{ M Ca(NO}_3)_2$ (Aldrich 99.997%) and 0.00675 M CaO (Aldrich 99.995%) with a total concentration of 0.05 M was filtered through a membrane filter (CaO was added to exchange solution to increase its pH because the frameworks of zeolite A crystals are usually destroyed by hydronium ions¹⁴).

Ion exchange was accomplished by allowing the solution to flow past each crystal at a velocity of approximately 1.0 cm/sec for 3 days at $19(1)^\circ\text{C}$. The crystal was placed in a finely drawn Pyrex capillary, attached to a vacuum system and cautiously dehydrated by gradually increasing its temperature (ca. 20°C/h) to 360°C at a constant pressure of $2 \times 10^{-6}\text{ Torr}$.

Finally, the system was maintained at the state for 48 h. After cooling to room temperature, the crystal, still under vacuum was sealed in its capillary by torch. The crystal was colorless.

To prepare the bromine complex, the crystal was treated with 180 Torr of zeolitically dried bromine vapor at 24°C ¹⁵. The colorless dehydrated crystal immediately became dark red. After about 30 min, the crystal, still in its bromine atmosphere, was sealed in its capillary by torch.

X-ray Data Collection

The space group $Pm\bar{3}m$ (no systematic absences) was used throughout this work for reasons discussed previously^{16,17}. 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 ($K_{\alpha 1}$, $\lambda = 0.70930\text{\AA}$; $K_{\alpha 2}$, $\lambda = 0.71359\text{\AA}$). The cell constant, as determined by a least-squares treatment of 25 intense reflections for which $19^\circ < 2\theta < 24^\circ$ is $12.211(2)\text{\AA}$ at $21(1)^\circ\text{C}$.

Reflections from two intensity-equivalent regions of reciprocal space (hkl , $h \leq k \leq l$ and lkh , $l \leq k \leq h$) were examined using the ω - 2θ scan technique. The data were collected using variable scan speeds; the maximum final scan time was 5 minutes per reflection. Most reflections were observed

at the slowest speeds, ranging between 0.13° and 0.29° in ω /min. The intensities of three reflections in diverse regions of reciprocal space were recorded every 3 hrs 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 WEIGHT¹⁸.

An absorption correction ($\mu R = 0.308$, $\rho_{\text{calc}} = 2.397$ g/cm³ and $F(000) = 892$) was judged to be negligible and was not applied¹⁹. Of the 865 pairs of reflections examined, only the 103 pairs whose net counts exceeded three times their corresponding esd's were used in structure solution and refinement.

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)] from the iodine sorption complexes of fully Ca(II)-exchanged zeolite A⁸. Anisotropic refinement of framework atoms converged to an R_1 index, $(\Sigma(F_o - |F_c|) / \Sigma F_o)$ of 0.295 and a weighted R_2 index, $(\Sigma w(F_o - |F_c|)^2 / \Sigma w F_o^2)^{1/2}$ of 0.398.

The initial difference Fourier function revealed one large peak at (0.193, 0.193, 0.193) of height 3.89(2) eÅ⁻³. Inclusion of this peak as Ca(1) lowered the error indices to $R_1 = 0.207$ and $R_2 = 0.206$ (see Table 1).

A subsequent difference Fourier synthesis revealed two large peaks at (0.138, 0.416, 0.5) and (0.277, 0.359, 0.5) with a peak height of 1.21(2) eÅ⁻² and 1.56(2) eÅ⁻³, respectively.

These peaks were stable in least-squares refinement. Including these peaks as Br(1) and Br(2) lowered the error indices to $R_1 = 0.149$ and $R_2 = 0.127$ (see Table 1).

A difference Fourier function revealed a peak at (0.166, 0.166, 0.166) with a height of 1.64(2) eÅ⁻³. Simultaneous positional, thermal, and occupancy refinement including this position converged to $R_1 = 0.128$ and $R_2 = 0.081$. The occupancy numbers at Br(1) and Br(2) refined to ca. 5.67(13) and 6.32(14) bromine atoms, respectively. These were reset and fixed at 6.0, the maximum number of atoms at each of these positions for packing reasons. It is furthermore reasonable that these two occupancies should be equal because the distance involved indicates that these positions represent dibromine molecules (see Table 1).

The final R values were $R_1 = 0.104$ and $R_2 = 0.112$. The final difference Fourier function was almost featureless except for an insignificant peak

Table 1. "Positional, Thermal and Occupancy Parameters

Atom	Wyc. Pos.	x	y	z	^b β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	"Occupancy varied fixed	
(Si, Al)	24(k)	0	1840(10)	3718(9)	54(8)	26(7)	32(8)	0	0	30(20)		^d 24.0
O(1)	12(h)	0	2260(30)	5000	130(50)	90(50)	20(30)	0	0	0		12.0
O(2)	12(i)	0	2880(30)	2880(30)	100(50)	60(20)	60(20)	0	0	150(60)		12.0
O(3)	24(m)	1170(10)	1170(10)	3350(20)	50(10)	50(10)	100(30)	-10(50)	10(40)	10(40)		24.0
Ca(1)	8(g)	2210(40)	2210(40)	2210(40)	170(40)	170(40)	170(40)	-50(80)	-50(80)	-50(80)	2.86(7)	3.0
Ca(2)	8(g)	1750(30)	1750(30)	1750(30)	60(20)	60(20)	60(20)	90(40)	90(40)	90(40)	3.12(9)	3.0
Br(1)	24(l)	1530(30)	4310(40)	5000	510(50)	900(100)	500(100)	-1230(90)	0	0	5.67(13)	6.0
Br(2)	24(l)	2750(50)	3900(70)	5000	270(80)	700(200)	1900(400)	-400(200)	0	0	6.32(14)	6.0

^aPositional 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. ^bThe anisotropic temperature factor = $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. ^cOccupancy factors given as the number of atoms or ions per unit cell. ^dOccupancy for (Si) = 12; occupancy for (Al) = 12.

Table 2. Selected Interatomic distances(Å) and angles(deg)

(Si, Al)-O(1)	1.65(2)
(Si, Al)-O(2)	1.64(2)
(Si, Al)-O(3)	1.70(1)
Ca(1)-O(3)	2.28(3)
Ca(2)-O(3)	2.20(3)
Br(2)-Br(1)	2.64(9)
Br(1)-O(1)	3.12(7)
O(1)-(Si, Al)-O(2)	110(2)
O(1)-(Si, Al)-O(3)	114(1)
O(2)-(Si, Al)-O(3)	102.2(9)
O(3)-(Si, Al)-O(3)	114(1)
(Si, Al)-O(1)-(Si, Al)	143(3)
(Si, Al)-O(2)-(Si, Al)	167(2)
(Si, Al)-O(3)-(Si, Al)	137(2)
O(3)-Ca(1)-O(3)	112(2)
O(3)-Ca(2)-O(3)	119(1)
O(1)-Br(1)-Br(2)	178(2)

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

at origin. This peak was not refined.

Atomic scattering factors for Ca^{2+} , O^- , Br^0 , and $(\text{Si, Al})^{1.75+}$ were used^{20,21}. The function describing $(\text{Si, Al})^{1.75+}$ 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^{22,23}. Bond lengths and selected angles are given in Table 2.

Discussion

In the bromine sorption complex of dehydrated $\text{Ca}_6\text{-A}$, 3 Ca^{2+} at Ca(1) and 3 Ca^{2+} at Ca(2) occupy 6-ring sites on the 3-fold axes of unit cell. Each Ca^{2+} ion at Ca(1) is *ca.* 0.673(25) Å into the large cavity side of (111) plane of 3 O(3)'s, whereas each Ca^{2+} ion at Ca(1) is recessed *ca.* 0.313(20) Å into the sodalite unit (see Table 3). Six dibromine molecules interact with O(1) framework oxygen (see Fig. 1 and 2) (The mean geometry of the structure is used in this discussion).

The Ca^{2+} ions at Ca(1) and Ca(2) are trigonally coordinated to their three nearest framework oxygens at O(3) at 2.28(3) Å and 2.20(3) Å, respectively.

Table 3. Deviations of atoms(Å) from the (111) plane at O(3)

O(3)	0.055(18)
Ca(1)	0.673(25)
Ca(2)	-0.313(20)

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

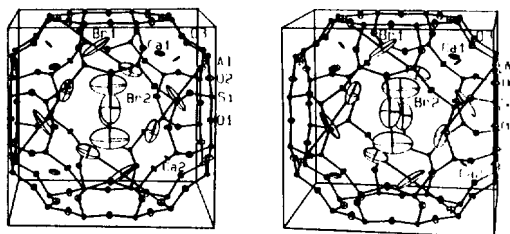


Fig. 1. The unit cell of bromine sorption complexes of the dehydrated $\text{Ca}_6\text{-A}$ is shown in stereoview. Three Ca^{2+} ions at Ca(1), three Ca^{2+} ions at Ca(2) and 6 dibromine molecules are shown. Ellipsoids of 20% probability are used.

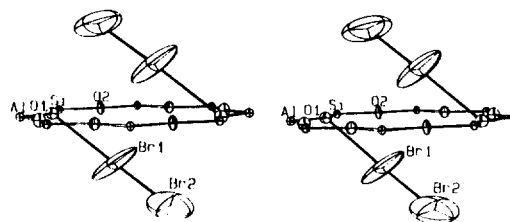


Fig. 2. Each 8-oxygen ring in the structure participates in a charge transfer interaction with two dibromines as shown. Ellipsoids of 20% probability are used.

vely. For comparison, the sum of the conventional ionic radii of Ca^{2+} and O^{2-} is 2.31 Å¹⁵.

In this structure, cations occupy only 6-ring sites; the 8-ring sites are empty. This occurs because the ionic radius of Ca^{2+} is relatively small. Larger cations such as Cs^+ ^{24,25}, K^+ ²⁶, Rb^+ ^{27,28}, and Tl^+ ^{29,30} preferentially occupy 8-ring sites.

Each Ca^{2+} ion at Ca(2) is located near the center of 6-ring on the 3-fold axis of the unit cell. The geometry about Ca^{2+} at Ca(2) is near-trigonal planar ($\text{O}(3)\text{-Ca}(2)\text{-O}(3) = 119(1)^\circ$).

In this work, bromine atoms have been found at two different 24-fold positions. These are interpreted to give two 24-fold molecular positions

which are occupied statistically by six dibromine molecules. Six molecules is the maximum number which can be accommodated at these sites; otherwise, unreasonably short Br-Br distances, corresponding to overlapping molecules, would result. For the 6.0 Br(1)-Br(2) molecules, the closest approach of Br(1) position to the framework is to O(1). The dibromine molecule acts as a Lewis acid with respect to the framework oxide ion at O(1) which has lone pair electrons. Furthermore, the O(1)-Br(1)-Br(2) angle $178(2)^\circ$ is close to linear. The bonding can be understood in terms of charge transfer complexation; the electronegative oxide ion at O(1) donates electron pair density axially to the vacant $4p\sigma^*$ antibonding molecule. Accordingly, the Br-Br bond order is reduced and the Br-Br bond is $2.64(9)$ Å. This bond length is reasonably longer than that in free dibromine, 2.29 Å³¹.

The Br(1)-O(1) approach distance, $3.12(7)$ Å, is less than the nonbonded approach distance 3.35 Å³², calculated from the sum of the appropriate nonbonded van der Waals radii. These Br(1)-O(1) distances indicate the existence of charge transfer complex between these dibromine molecules and framework oxide ions at O(1). However, the sorption of bromine has little effect on the framework structure of zeolite compared with that of dehydrated $\text{Ca}_6\text{-A}^8$.

Recently, the crystal structure of a bromine sorption complex of partially cobalt(II)-exchanged zeolite A has been determined⁴. In this structure, a redox reaction has apparently occurred between Co(II) and Br_2 to yield Co(III) and Br_3^- ions. The 4 Na^+ and 4 Co^{3+} ions per unit cell occupy 6-ring sites on 3-fold axes. Each Na^+ ion is recessed *ca.* 0.33 Å into the sodalite unit, whereas each Co^{3+} ion is *ca.* 0.54 Å on the large-cavity side of the plane of its 3 coordinating oxygens. Four quite asymmetric Br_3^- ions, each bridges between a Co^{3+} ion and an 8-ring framework oxygen (Co-Br-Br) = 116° , (Br-Br-Br) = 138° , and Br-Br-O = 177° ; the corresponding Co-Br-Br-Br-O distances are $2.59(1)$, $2.28(1)$, $2.64(3)$, and $3.40(2)$ Å, respectively). The near-linear Br-Br-O angle is indicative

of a charge-transfer interaction. Two other bromine molecules similarly form charge-transfer complexes with 8-ring oxygens. However, in this work, the closest approach distance of a bromine atom to Ca^{2+} ion is $4.04(1)$ Å (see Fig. 1 and 2). Therefore, dibromine molecule makes no significant approach to Ca^{2+} ions.

The present structure is very similar to the structure of a iodine sorption complex of dehydrated $\text{Ca}_6\text{-A}^8$. In this structure, six divalent Ca^{2+} ions are located on three different threefold axes associated with 6-ring oxygens. Also, 6.0 diiodine molecules per unit cell are sorbed. Each iodine molecule makes a close approach, along its axis to framework oxygen atom, with I-I distance of $2.72(2)$ Å, I-O distance of $3.32(3)$ Å, and I-I-O = 180° . The structure also indicates that diiodine molecule forms charge transfer complex with framework oxygen.

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1. The nomenclature refers to the contents of the unit cell. For example, $\text{Na}_{12}\text{-A}$ represents $\text{Na}_{12}\text{Si}_{12}\text{Al}_{12}\text{O}_{48}$.
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