

Crystal Structure of a Bromine Sorption Complex of Dehydrated Calcium and Silver Exchanged Zeolite A

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칼슘 및 은 이온으로 치환된 제올라이트 A를 탈수한 후 브롬을 흡착한 결정구조

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Abstract

The crystal structure of a bromine sorption complex of vacuum-dehydrated Ag^+ and Ca^{2+} exchanged zeolite A ($a=12.234(1) \text{ \AA}$) has been determined by single-crystal X-ray diffraction methods in the cubic space group $Pm\bar{3}m$. The crystal was prepared by flow method using exchange solution in which mole ratio of AgNO_3 and $\text{Ca}(\text{NO}_3)_2$ was 1:150 with a total concentration of 0.05 M. The crystal was dehydrated at 360°C and 2×10^{-6} Torr for 2 days, followed by exposure to 180 Torr of Br_2 vapor for 20 min. Full-matrix least-squares refinements converged to the final error indices of $R_1=0.111$ and $R_2=0.101$ using 90 reflections for which $I>3\sigma(I)$. About 3.1 Ag^+ ions and 4.45 Ca^{2+} ions lie on the two crystallographically nonequivalent three-fold axes associated with 6-ring oxygens. A total of six bromine molecules are sorbed per unit cell. Each bromine molecule approaches a framework oxide ions axially ($\text{Br-Br-O}=171(2)^\circ$, $\text{O-Br}=3.25(6) \text{ \AA}$; and $\text{Br-Br}=2.61(8) \text{ \AA}$) by a charge-transfer interaction.

요 약

Ag^+ 이온과 Ca^{2+} 이온으로 교환하고 진공 탈수한 제올라이트 A에 브롬을 흡착한 결정 구조($a=12.234(1) \text{ \AA}$)를 입방공간군 $Pm\bar{3}m$ 을 사용하여 단결정 X-선 회절법으로 구조를 해석하였다. 결정은 AgNO_3 와 $\text{Ca}(\text{NO}_3)_2$ 의 몰 비를 1:150으로 하고 농도를 0.05 M으로 한 혼합용액을 사용하여 흐름법으로 3일간 이온 교환하였다. 그 결정을 360°C 에서 2×10^{-6} Torr하에서 2일간 진공 탈수한 다음 약 180 Torr의 브롬 기체로 24°C 에서 20분간 처리하였다. 이 결정 구조는 Full-matrix 최소자승법 정밀화 계산에서 $I>3\sigma(I)$ 인 반사 90개를 써서 $R_1=0.111$, $R_2=0.101$ 까지 얻었다. 이 구조에서 3.1개의 Ag^+ 이온과 4.45개의 Ca^{2+} 이온이 6-링 산소와 결합하면서 두 개의 서로 다른 3회 회전축 상에 위치하고 있었고 단위 세포당 총 여섯 분자의 브롬이 흡착되었다. 각 브롬 분자는 골격 구조의 산소 이온과 전하 이동 작용에 의해 결합하고 있었다($\text{Br-Br-O}=171(2)^\circ$, $\text{O-Br}=3.25(6) \text{ \AA}$; $\text{Br-Br}=2.61(8) \text{ \AA}$).

Introduction

Zeolite are high capacity and highly selective sorbents due to the presence of channels in their structures. A zeolite single crystal can readily be

maintained inside a pyrex capillary throughout ion-exchange, dehydration, and sorption process, without being exposed to the atmosphere or to solvent interferences. Therefore, a large number of sorption complexes can be studied in the com-

plete absence of competitive ligands. The structural informations of absorbed guest molecules in the inner surface of the zeolite A have been obtained by X-ray crystallographic methods.

The crystal structures of a bromine sorption complex of $\text{Na}_{12}\text{-A}$ ^{1,2)} and of a similar iodine sorption complex of $\text{Ca}_4\text{Na}_4\text{-A}$,³⁾ have been reported. In the crystal structure of a bromine sorption complex of $\text{Na}_{12}\text{-A}$,^{1,2)} about six bromine molecules per unit cell were sorbed. However, it was reported that these bromine molecules interacted neither with the anionic framework nor with the eight of the 12 Na^+ ions which were located.

Several structures of Br_2 and Cl_2 sorption complexes of Ag^+ ,⁴⁾ Eu(II) ,⁵⁾ and Co(II) -exchanged⁶⁾ zeolite A have been determined. When Br_2 gas was sorbed onto a single crystal of vacuum-dehydrated $\text{Ag}_{12}\text{-A}$,⁷⁾ six bromine molecules are sorbed per unit cell; 3.6 Br_2 molecules coordinate to draw the 3.6 of the eight 6-ring Ag^+ ions into large cavity, and 2.4 Br_2 molecules form charge transfer complexes with framework oxygen ($\text{O-Br-Br}=174(4)^\circ$).

In the structures of chlorine sorption complexes of Eu(II) -exchanged zeolite-A⁵⁾ and Ag^+ -exchanged zeolite A,⁸⁾ chlorine gas is reported to oxidize Eu(II) to Eu(IV) and hexasilver to AgCl . In the latter structure, an additional six chlorine molecules are sorbed per unit cell ($\text{O-Cl-Cl}=166(2)^\circ$). When Cl_2 gas was sorbed onto a single-crystal of vacuum-dehydrated $\text{Co}_4\text{Na}_4\text{-A}$, chlorine⁹⁾ molecules coordinated to the Co(II) ion in a bent manner. The chlorine molecule is essentially basic with respect to the hard acid Co(II) and the Cl-Cl bond is lengthened by a large amount, approximately 0.5 \AA , upon complexation.

This work was undertaken to investigate bromine sorption by dehydrated Ag^+ and Ca^{2+} ion-exchanged zeolite A and to determine the positions of sorbed bromine molecules.

Experimental Section

Crystals of zeolite 4A were prepared by the

inclusion of seed crystals from the previous preparation. A single crystal of zeolite 4A ($\text{Na}_{12}\text{-A}$), 0.085 mm on an edge, was selected and lodged in a fine glass capillary. The crystal was prepared by using exchange solution in which mole ratio of AgNO_3 (Aldrich, 99.999%) and $\text{Ca(NO}_3)_2$ (Aldrich, 99.999%) was 1:150 with a total concentration of 0.05 M. The single crystal was then ion-exchanged by the flow method. The exchange solution was allowed to flow past the crystal at about 1.2 cm/sec for three days.

After the single crystal was ascertained that it was wedged firmly between the capillary walls, the tip of the capillary was sealed with a small flame by torch. The capillary tube was then attached to the line of pyrex vacuum system. The clear, colorless, hydrated Ag^+ and Ca^{2+} -exchanged crystal was dehydrated for 2 days at 360°C and 2×10^{-6} Torr. To prepare the bromine sorption complex, the crystal was treated with 180 Torr of zeolitically dried bromine vapor. The colorless, dehydrated crystal immediately became dark red and continued to darken with time. After about 20 min at 24°C , the crystal, still in its bromine atmosphere, was sealed in its capillary by torch.

X-ray Data Collection

The cubic space group $Pm\bar{3}m$ (no systematic absences) was used instead of $Fm\bar{3}c$ for reasons described previously.^{11,12)} 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 $\text{K}\alpha$ radiation ($\text{K}\alpha_1$, $\lambda=0.70930 \text{ \AA}$; $\text{K}\alpha_2$, $\lambda=0.71359 \text{ \AA}$) was used for all experiments. The unit cell constant, as determined by a least-squares refinement of 25 intense reflections for which $19^\circ < 2\theta < 24^\circ$ was $12.234(1) \text{ \AA}$. Reflections from two intensity-equivalent regions of reciprocal space (hkl , $h \leq k \leq l$: hkl , $h \leq l \leq k$) were examined by us-

ing the ω - 2θ scan technique. The data were collected by using variable scan speeds. The maximum final scan time is 5 min per one reflection. Most reflections were observed at slow scan speeds, from 0.15 to 0.26 deg min⁻¹ in ω .

The intensities of three reflections in diverse regions of the reciprocal space were recorded every 3 h to monitor crystal and instrument stability. For each region of the reciprocal space, the intensities of all lattice points for which $2\theta < 70^\circ$ were recorded.

The raw data for each region were corrected for Lorentz and polarization effects due to incident beam monochromatization; the reduced intensities were merged and resultant estimated standard deviations were assigned to each average reflection by the computer programs, PAINT and WEIGHT.¹³⁾ The absorption correction was judged to be negligible and was not applied.¹⁴⁾ Of the 384 pairs of reflections for bromine sorption complex of Ag_{3.1}Ca_{4.45}-A, only the 90 reflections with $I > 3\sigma(I)$ were used in the subsequent structure determination.

Structure Determination

Full matrix least-squares refinement was initiated by using the atomic parameters of the framework atoms ((Si, Al), O(1), O(2) and O(3)) determined previously for the iodine sorption

complexes of fully Ca(2)-exchanged zeolite A.¹⁵⁾ Anisotropic refinement quickly converged to the error indices, $R_1 = \Sigma |F_o - |F_c|| / \Sigma F_o = 0.40$ and $R_2 = (\Sigma \omega(F_o - |F_c|)^2 / \Sigma \omega F_o^2)^{1/2} = 0.53$.

A difference Fourier function revealed two large threefold axes peaks at (0.221, 0.221, 0.221) and (0.166, 0.166, 0.166) with a peak height of 6.54 eÅ⁻³ and 4.27 eÅ⁻³, respectively.

A subsequent difference Fourier function revealed two peaks at (0.11, 0.45, 0.5) and (0.22, 0.36, 0.5). Anisotropic refinements of the framework atoms, and isotropic refinements of Ag(1) and Ca(1), and these positions as positions of bromine atoms converged to $R_1 = 0.122$, and $R_2 = 0.109$. Anisotropic refinements including Ag(1), Ca(1), Br(1), and Br(2) positions converged to $R_1 = 0.115$ and $R_2 = 0.102$. The occupancies of these cations per unit cell refined to Ag(1)=3.09(2) and Ca(1)=4.46(27). These were fixed at Ag(1)=3.1 and Ca(1)=4.45 because the cationic charge should not exceed +12 per $Pm\bar{3}m$ unit cell. Successive refinements indicated that the atoms at Br(1) and Br(2) were bromine molecules (Br(1)-Br(2)=2.61(8) Å).

The occupancy numbers at Br(1) and Br(2) refined to *ca.* 5.63(28) and 5.81(27) 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 furth-

Table 1. ^aPositional, ^bThermal, and Occupancy Parameters Dehydrated Ag_{3.1}Ca_{4.45}-A absorbed Br₂ molecules

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	1850(10)	3715(9)	53(9)	13(8)	0	0	0	10(2)		24.0 ^a
O(1)	12(h)	0	2050(20)	5000	140(50)	30(30)	0	0	0	0		12.0
O(2)	12(i)	0	2860(30)	2860(30)	100(50)	70(30)	0	0	0	130(70)		12.0
O(3)	24(m)	1138(2)	1140(20)	3430(20)	30(10)	60(30)	100(30)	10(40)	10(40)	10(40)		24.0
Ag(1)	8(g)	2260(10)	2260(10)	2260(10)	57(7)	57(7)	60(20)	60(20)	60(20)	60(20)	3.09(2)	3.1
Ca(1)	8(g)	1720(20)	1720(20)	1720(20)	80(20)	80(20)	-10(40)	-10(40)	-10(40)	-10(40)	4.46(27)	4.45
Br(1)	24(l)	1100(30)	4470(40)	50000	390(70)	330(70)	0	-500(100)	0	0	5.63(28)	6.0
Br(2)	24(l)	2270(50)	3740(50)	50000	954(200)	1883(400)	0	-2022(500)	0	0	5.81(27)	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 are given as the number of atoms or ions per unit cell.

^dOccupancy for (Si)=12; occupancy for (Al)=12.

ermore reasonable that these two occupancies should be equal because the distance involved indicates that these positions represent bromine molecules (see Table 1). The O(3)-Br(1)-Br(2) angle is $171.0(2)^\circ$, indicating that Br₂ molecule has formed a charge transfer complex with a framework oxide ion.

The final error indices converged to $R_1=0.111$ and $R_2=0.101$. The final difference Fourier function was almost featureless except for an insignificant at origin. This peak was not refined. Final positional, thermal, and occupancy parameters are presented in Table 1; bond angles are given in Table 2.

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

(Si, Al)-O(1)	1.590(10)	O(3)-Ag(1)-O(3)	110.3(5)
(Si, Al)-O(2)	1.620(20)	O(3)-Ca(1)-O(3)	117.4(8)
(Si, Al)-O(3)	1.680(10)	O(3)-Br(1)-Br(2)	171.0(2)
Ag(1)-O(3)	2.42(3)		
Ca(1)-O(3)	2.32(3)		
Br(1)-O(1)	3.25(6)		
Br(1)-Br(2)	2.61(8)		
O(1)-(Si, Al)-O(2)	121.0(2)		
O(1)-(Si, Al)-O(3)	107.0(1)		
O(2)-(Si, Al)-O(3)	104.9(9)		
O(3)-(Si, Al)-O(3)	112.0(2)		
(Si, Al)-O(1)-(Si, Al)	162.0(2)		
(Si, Al)-O(2)-(Si, Al)	171.0(2)		
(Si, Al)-O(3)-(Si, Al)	144.0(1)		

^aNumbers in parentheses are estimated standard deviations in the least significant digit given for the corresponding value.

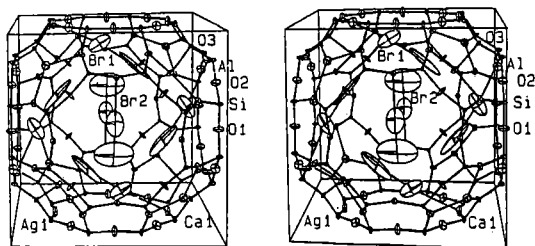


Fig. 1. A stereoview of the large cavity of bromine sorption complexes of dehydrated $\text{Ag}_{3.1}\text{Ca}_{4.45}\text{-A}$. Four Ag^+ ions Ag(1), four Ca^{2+} ions at Ca(1) and six bromine molecules are shown. About 55% of unit cell may have this conformation. Ellipsoids of 20% probability are used.

Discussion

In the bromine sorption complex of dehydrated $\text{Ag}_{3.1}\text{Ca}_{4.45}\text{-A}$, about 3.1 Ag^+ ions at Ag(1) and 4.45 Ca^{2+} ions at Ca(1) occupy 6-ring sites on the threefold axes of the unit cell (see Fig. 1). Each Ag^+ ion at Ag(1) is recessed ca. $0.769(7)$ Å into the sodalite unit cell and each Ca^{2+} ion at Ca(1) extends $0.379(14)$ Å into the large cavity side from the (111) plane at O(3)'s (see Table 3). The Ag(1)-O(3) distance is $2.42(3)$ Å less than the sum of the conventional ionic radii of Ag^+ and O^{2-} , 2.58 Å. In this structure, the Ca(1)-O(3) distance, ca. $2.32(3)$ Å, is almost the same

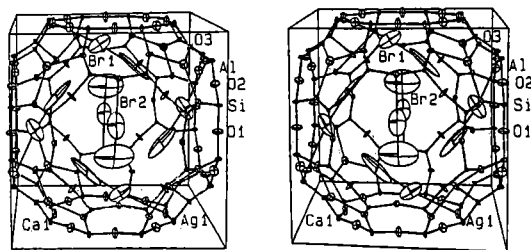


Fig. 2. A stereoview of the large cavity of bromine sorption complexes of dehydrated $\text{Ag}_{3.1}\text{Ca}_{4.45}\text{-A}$. Two Ag^+ ions at Ag(1), five Ca^{2+} ions at Ca(1), and six bromine molecules are shown. About 45% of unit cell may have this conformation. Ellipsoids of 20% probability are used.

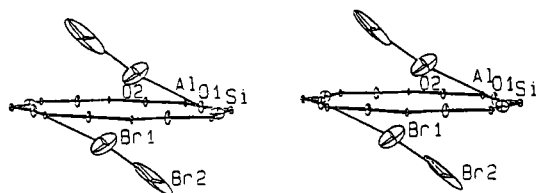


Fig. 3. A stereoview of the structure about an 8-ring. Each 8-oxygen ring in the structure participates in a charge transfer interaction with two dibromines as shown. Ellipsoids of 10% probability are used.

Table 3. Deviation of atom (Å) from the (111) plane at O(3)

O(2)	$-0.011(19)^a$
Ag(1)	$-0.769(7)$
Ca(1)	$-0.379(14)$

^aNegative deviation indicates that the atom lies on the same side of the plane as the origin.

as the sum of the conventional ionic radii of Ca^{2+} and O^{2-} , 2.31 Å.¹⁶⁾ The geometry about Ca^{2+} at Ca(1) is near-trigonal planar with O(3)-Ca(1)-O(3)=117.4 (8)° (see Table 2).

In this work, bromine atoms have been found at two different 24-fold molecular positions which are occupied statistically by six bromine molecules. Six is the maximum number which can be accommodated at these sites. The closest approach of Br(1) position to the framework is to O(1) position. The bromine molecule acts as a Lewis acid with respect to the framework oxide ion at O(1) which has lone pair electrons. This bonding can be understood in terms of charge transfer complexation because the electronegative oxide ion at O(1) donates electron pair density axially to the vacant $4p\sigma^*$ antibonding orbital of the Br atom. Accordingly, the Br-Br bond order is reduced and the Br-Br bond is 2.61(8) Å, which is reasonably longer than Br-Br bond in free bromine, 2.29 Å.

The Br(1)-O(1) approach is 3.25(6) Å, less than the nonbonded approach distance, 3.35 Å, calculated from the sum of the appropriate nonbonded van der Waals radii.¹⁷⁾ However, the sorption of bromine has little effect on the framework structure of zeolite compared with that of dehydrated $\text{Ag}_3\text{Ca}_{4.45}\text{-A}$. The near-linear Br-Br-O angle (Br-Br-O=171(2)°) also indicates charge transfer interaction. In this structure, the closest approach distance of a bromine atom to an Ag^+ ion is 3.81 Å and this to Ca^{2+} ion is 4.76 Å. Therefore, bromine molecule makes no significant approach to Ag^+ and Ca^{2+} ions.

In summary, all cations are located on two different threefold axes associated with 6-ring oxygens. Also, six bromine molecules are sorbed per unit cell. Each bromine molecule makes a close approach, along its axis to framework oxygen atom, with Br-Br distance of 2.6(8) Å, Br-O distance of 3.25(6) Å, and Br-Br-O=171(2)°. This structure indicates that bromine molecule

forms charge transfer complex with framework oxygen.

Acknowledgement

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References

- 1) This nomenclature refers to the contents of the unit cell. For example, $\text{Na}_{12}\text{-A}$ represents $\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}$, exclusive of water molecules if a hydrated crystal is considered.
- 2) Meier, W. M. and Shoemaker, D. P. *Z. Kristallogra.* **126** (1966), 357.
- 3) Seff, K. and Shoemaker, D. P. *Acta Crystallogra.* **22** (1967), 162.
- 4) Kim, Y. and Seff, K. *J. Am. Chem. Soc.* **100** (1978), 1071.
- 5) Prior, R. L. and Seff, K. *J. Am. Chem. Soc.* **100** (1978), 976.
- 6) Subramanian, V., Seff, K. and Ottersen, T. *J. Am. Chem. Soc.* **100** (1978), 2911.
- 7) Kim, Y. and Seff, K. *J. Phys. Chem.* **82** (1978), 925.
- 8) Kim, Y. and Seff, K. *J. Am. Chem. Soc.* **100** (1978), 3801.
- 9) Kim, Y. and Seff, K. *J. Phys. Chem.* **82** (1978), 921.
- 10) Charnell, J. F. *J. Cryst. Growth* **8** (1971), 291.
- 11) Seff, K. *J. Phys. Chem.* **76** (1972), 2601.
- 12) Seff, K. and Mellum, M. D. *J. Phys. Chem.* **88** (1984), 3560.
- 13) Principal computer programs used in this study were "Structure Determination Package Programs" written by Frenz, B. A. and Okaya, Y. These programs were supplied by Enraf-Nonius, Netherlands, 1987.
- 14) Prior, R. L. and Seff, K. *J. Am. Chem. Soc.* **99** (1977), 6249.
- 15) Jang, S. B., Han, Y. W., Kim, D. S. and Kim, Y. *Korea J. Cryst.* **1** (1990), 76.
- 16) *Handbook of Chemistry and Physics*, 70th Ed.; The Chemical Rubber Co., Cleveland, Ohio, 1989/1990, p.F-187.
- 17) Reference 16, p.D-190.