

Ag⁺ 이온과 Ca²⁺ 이온으로 치환한 제올라이트 A를 탈수한 후 요오드를 흡착한 결정구조

배명남, 김 양, 김은식
부산대학교 화학과

The Crystal Structure of an Iodine Sorption Complex of Dehydrated Calcium and Silver Exchanged Zeolite A

Myung Nam Bae, Yang Kim, and Un Sik Kim
Department of Chemistry, Pusan National University,

요 약

Ag⁺ 이온과 Ca²⁺ 이온으로 교환하고 진공 탈수한 제올라이트 A에 요오 드를 흡착한 결정 구조($a = 12.174(3)$ Å)를 21 °C에서 입방공간군 $Pm\bar{3}m$ 을 사용하여 단결정 X-선 회절법으로 구조를 해석하였다. 결정은 AgNO₃와 Ca(NO₃)₂의 몰비를 1 : 150으로 하고 농도를 0.05 M로 한 혼합용액을 사용해 흐름법으로 3 일간 이온 교환한 후 360 °C에서 2×10^{-6} Torr 하에서 2 일간 진공 탈수한 후 80°C에서 14.3 Torr의 요오드 증기로 24 시간 처리하였다. 결정 구조는 Full-matrix 정밀화 계산에서 $I > 3\sigma(I)$ 인 122개의 독립 반사를 사용하여 최종 오차 지수 $R_1 = 0.082$, $R_2 = 0.068$ 까지 정밀화시켰다. 본 결정 구조에서는 단위세포당 결정학적으로 세 가지의 다른 종류의 양 이온 즉 2 개의 Ag⁺ 이온, 1.1 개의 Ag⁺ 이온 그리고 4.45 개의 Ca²⁺이온이 6-링의 산소와 결합하면서 각각 서로 다른 3 회 회전축 상에 위치하고 있었다. 2.0 개의 Ag⁺ 이온이 3개의 산소로 만들어지는 (111) 평면으로부터 큰 동공 쪽으로 1.399(4) Å 떨어져 위치하고 있었다. 또 다른 1.1 개의 Ag⁺ 이온은 반대쪽에서 발견되었다. 여섯 분자의 요오드 분자가 흡착되었다. 각 요오드 분자는 골조 산소와 전하이동 착물을 형성하였다 (O-I = 3.43(2) Å, I-I = 2.92 Å, I-I-O ; 166.1(3)°). 이중 2개의 요오드 분자는 각각 하나의 Ag⁺ 이온과 매우 가깝게 결합하고 있음을 알 수 있었다 (Ag-I ; 2.73 Å).

Abstract

The crystal structure of an iodine sorption complex of vacuum-dehydrated Ag⁺ and Ca²⁺ exchanged zeolite A ($a = 12.174(3)$ Å) has been determined at 21°C by single-crystal X-ray diffraction techniques in the cubic space group $Pm\bar{3}m$. The crystal was prepared by flow method for three days using exchange solution in

solution in which mole ratio of AgNO₃ and Ca(NO₃)₂ was 1 : 150 with total concentration of 0.05 M. The complex was prepared by dehydration at 360 °C and 2 X 10⁻⁶ Torr for 2 days, followed by exposure to about 14.3 Torr of iodine vapor at 80 °C for 24 hours. Full-matrix least-squares refinement converged to the final error indices of R1 = 0.082, R2 = 0.068 using 122 reflections for which I > 3σ(I). Two Ag⁺ ions, 1.1 Ag⁺ ions, and 4.45 Ca²⁺ ions per unit cell are located on three different three-fold axes associated with 6-ring oxygens. Two Ag⁺ ions per unit cell are in the large cavity, 1.399(4) Å from the (111) plane of three oxygens. Another 1.1 Ag⁺ ions are found at opposite sites. Six iodine molecules are sorbed per unit cell. Each I₂ molecule approaches a framework oxide ion axially (I-I-O = 166.1(3)°, O-I = 3.43 Å and I-I = 2.92(2) Å), by a charge transfer complex interaction. Two Ag⁺ ions make a close approach to the iodine molecules (Ag-I ; 2.73(2) Å).

1. Introduction

In the crystal structure of an iodine sorption complex of Ca₄Na₄-A^{1,2)} and that of a bromine sorption complex of dehydrated fully Ag⁺-exchanged zeolite A,³⁾ the halogen molecules interact with oxide ions of the zeolite framework. In these structures, Br₂ and I₂ molecules act as Lewis acids with respect to the lone pairs of framework oxide ion. Halogen molecules form linear charge transfer complexes to framework oxide ions. However, in the structure of a bromine sorption complex of Na₁₂-A,⁴⁾ six dibromine molecules were sorbed per unit cell, and they appeared to interact neither with the anionic framework nor with Na⁺ ions. When Cl₂ gas was sorbed onto a single crystal of vacuum-dehydrated Co₄Na₄-A,²⁾ dichlorine molecules coordinated to Co(II) ion in a bent manner. The dichlorine bond is lengthened by a large amount, approximately 0.5 Å, upon complexation.⁵⁾ In the crystal structures of iodine sorption complexes of Co_{3.5}Na₅-A,⁶⁾ 2.5 iodine molecules per unit cell were sorbed at 70 °C within 30 minutes and 5 iodine molecules per unit cell were sorbed at 80 °C within 24 hours. Each iodine molecule makes a close linear approach, along its axis to framework oxygen atom with I-I-O = 175°.

This work was undertaken to determine the positions and chemical bonds of the sorbed iodine molecules and cations within the dehydrated Ca²⁺- and Ag⁺-exchanged zeolite A.

2. Experimental Section

Single crystal of the synthetic molecular sieve 4A, Na₁₂-A,²⁾ were prepared by Chamell's method.⁷⁾ A single crystal about 0.085 mm on an edge was lodged in a fine glass capillary for ion exchange. A crystal of Ag_{3.1}Ca_{4.5}-A was prepared using exchange solution of AgNO₃ (Aldrich, 99.999%) and Ca(NO₃)₂·H₂O (Aldrich, 99.999%) in the mole ratio of 1 to 150, with a total concentration of 0.05 M.

Ion exchange was accomplished by allowing the solution to flow past the crystal at about 1.0 cm/sec for three days. The crystal remained clear and colorless. The hydrated Ag_{3.1}Ca_{4.5}-A crystal was dehydrated for 2 days at 360 °C and 2 X 10⁻⁶ Torr. To prepare the iodine complex, the dehydrated Ag_{3.1}Ca_{4.5}-A crystal was treated with zeolitically dried I₂ vapor at 80 °C (vapor pressure of I₂ at 80 °C is 14.3 Torr) for 24 hours. The resultant crystal became black after exposure to iodine vapor. Finally, the crystal in iodine atmosphere was sealed in its capillary.

3. X-ray Data Collection

The cubic space group $Pm\bar{3}m$ (no symmetric absences) was used instead of $Fm\bar{3}c$ for reason described previously.^{8,9)} Preliminary crystallographic experiments and subsequent data collection were performed with an automated, four-circle Enraf Nonius CAD-4 diffractometer, equipped with a graphite monochromator and a PDP micro 11/73 computer. Molybdenum $K\alpha_1$, $\lambda=0.70930$ Å, $K\alpha_2$, $\lambda=0.71359$ Å) was used for all experiments. The unit cell constant, $a = 12.174(3)$ Å, was determined by a least-squares treatment of 25 intense reflections for which $18^\circ < 2\theta < 24^\circ$. The data were collected by using variable scan speeds. Most reflections observed at slow scan speeds, ranging between 0.15° and 0.26° in ω/min . The intensities of three reflections in diverse region 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 collections. The intensities

of all lattice points for which $2\theta < 70^\circ$ were recorded.

The raw data were corrected Lorentz and polarization effects, including that due to incident beam monochromatization assuming the monochromator crystal to be half mosaic and half perfect in character. The resultant estimated standard deviations were assigned to each reflection by the computer program, PAINT and WEIGHT.¹⁰⁾ An absorption correction ($\mu R = 0.028$) was not applied.¹¹⁾ Of the 590 reflections, only the 122 reflections for which $I < 3\sigma(I)$ were used in subsequent structure determinations.

4. 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)] from the iodine sorption complexes of fully Ca(II)-exchanged zeolite A.¹²⁾ Anisotropic refinement of framework atoms and isotropic refinement of Ag^+ positions converged to an R_1 index, $(\sum |F_o - F_c| / \sum F_o)$ of 0.39 and a weighted R_2 index, $(w(F_o - F_c)^2 / \sum w F_o^2)^{1/2}$ of 0.362. A difference

Table I. ^aPositional, Thermal, and Occupancy Parameters of Dehydrated $\text{Ag}_{31}\text{Ca}_{445}\text{-A}$ sorbed 6I2 molecules.

Atom	Wyc. Pos.	x	y	z	^b β_{11} ^c B_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	^c Occupancy varied fixed	
(Si,Al)	24(k)	0	1834(7)	3704(6)	42(5)	7(4)	-2(4)	0	0	20(10)	24d	
O(1)	12(h)	0	2080(20)	5000	70(30)	50(30)	40(20)	0	0	0	12.0	
O(2)	12(i)	0	2900(20)	2900(20)	150(40)	60(20)	60(20)	0	0	90(50)	12.0	
O(3)	24(m)	1090(10)	1090(10)	3400(10)	80(10)	80(10)	-10(10)	60(30)	-10(20)	-10(20)	24.0	
Ag(1)	8(g)	2523(7)	2523(7)	2523(7)	24(4)	24(4)	24(4)	-40(10)	-40(10)	-40(10)	2.00(7)	2.0
Ag(2)	8(g)	1800(20)	1800(20)	1800(20)	150(20)	150(20)	150(20)	-80(50)	-80(50)	-80(50)	1.09(9)	1.1
Ca(1)	8(g)	2239(9)	2239(9)	2239(9)	3.2(5) ^e						4.46(9)	4.45
I(1)	24(l)	1510(10)	4458(9)	5000	230(20)	210(20)	140(10)	-20(30)	0	0	5.80(20)	6.0
I(2)	24(l)	2860(10)	3650(10)	4440(10)	230(20)	190(20)	210(20)	0	-240(30)	-200(30)	5.80(20)	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. ^eIsotropic thermal parameter in units of \AA^2 .

Fourier function revealed one large threefold axis peak at (0.253, 0.253, 0.253) of height 2.9(7) eÅ⁻³ as Ag(1) positions (see Table I).

It is not difficult to distinguish Ca²⁺ from Ag⁺ ions for several reasons. Firstly, their atomic scattering factors are quite different, 46 e⁻ for Ag⁺ vs. 18 e⁻ for Ca²⁺. Secondly, their ionic radii are different, Ca²⁺ = 0.99 Å and Ag⁺ = 1.26 Å¹⁹. Also, the approach distances between Ag⁺ and zeolite oxygens have been determined in the previous structure²⁰ and are indicative.

Finally, the requirement that the cationic charges sum to +12 per unit cell does not allow the major positions to refine to acceptable occupancies with an alternative assignment of ionic identities.

A subsequent difference Fourier function was revealed peaks at (0.15, 0.15, 0.15), (0.18, 0.18, 0.18), and (0.15, 0.45, 0.5). The first one was unstable in later least-squares refinement. Isotropic refinement of the latter three positions as Ag(2), and I(2), together with anisotropic refinement of the framework atoms and Ag(1), converged to R₁ = 0.141 and R₂ = 0.147. Successive difference Fourier map revealed two peaks at (0.22, 0.22, 0.22) and (0.26, 0.36, 0.44) of

heights 1.0(9) and 1.5(4) eÅ⁻³, respectively. The first refined as 4.45 Ca²⁺ ions and the second one as iodine atom of 5.8 I(2). The isotropic refinement of Ca(1) and Ag(2), together with anisotropic refinement all other atoms, converged to R₁ = 0.083 and R₂ = 0.069. The occupancy refinement of Ag(1) and Ag(2) converged at 2.0 and 1.09 Ag⁺ ions, respectively. These values were reset and fixed at 2.0 and 1.1 Ag⁺ ions, respectively (see Table I). The occupancy numbers at I(1) and I(2) refined to ca. 5.60(20) and 5.80(20), respectively.

However, the maximum number of molecules which can be associated with the 8-ring oxide ions is six and these two numbers were reset and fixed at 6.0. These indicate that the atoms at I(1) and I(2) are diiodine molecules (I(1)-I(2) = 2.92(2) Å) (see Table II). The final error indices converged to R₁ = 0.082, and R₂ = 0.068.

Atomic scattering factors for Ag⁺, Ca²⁺, O⁻, and (Si,Al)^{1.75+} were used.^{13,14} The function describing (Si,Al)^{1.75+} is the mean of the Si⁰, Si⁴⁺, Al⁰, and Al³⁺ functions. All scattering factors were modified to account for the real component (Δf) of the anomalous dispersion correction.^{15,16}

Table II. Selected Interatomic Distances(Å) and Angles(deg)^a of Ag₃₁Ca_{4.45}6I₂.

(Si,Al)-O(1)	1.606(9)	(Si,Al)-O(1)-(Si,Al)	157.8(9)
(Si,Al)-O(2)	1.620(10)	(Si,Al)-O(2)-(Si,Al)	154.5(6)
(Si,Al)-O(3)	1.648(9)	(Si,Al)-O(3)-(Si,Al)	147.0(2)
Ag(1)-O(3)	2.69(1)	O(3)-Ag(1)-O(3)	100.3(2)
Ag(2)-O(3)	2.30(2)	O(3)-Ca(1)-O(3)	119.8(6)
Ca(1)-O(3)	2.43(1)	O(3)-Ag(2)-O(3)	119.7(3)
Ag(1)-I(2)	2.73(2)	O(3)-Ca(1)-O(3)	109.7(3)
I(1)-O(1)	3.43(2)	O(1)-I(1)-I(2)	166.1(3)
I(1)-I(2)	2.92(2)	I(1)-I(2)-Ag(1)	104.9(6)
O(1)-(Si,Al)-O(2)	116.8(2)		
O(1)-(Si,Al)-O(3)	108.9(8)		
O(2)-(Si,Al)-O(3)	107.8(8)		

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

The final positional, thermal, and occupancy parameters are presented in Table I. Interatomic distances and angles are given in Table II.

5. Discussion

In the structure of the iodine sorption complex of dehydrated $\text{Ag}_{3.1}\text{Ca}_{4.45}\text{-A}$, 2 Ag^+ ions at Ag(1), 1.1 Ag^+ ions at Ag(2), and 4.45 Ca^{2+} ions at Ca(1) occupy 6-ring sites on the threefold axes of unit cell (see Figure 1). The fractional occupancies observed at Ag(1), Ag(2), and Ca(1) indicate the existence of at least two types of unit cells with regard to the cations. About 55 % of the unit cells may have 2 Ag^+ ions at Ag(1), 2 Ag^+ ions at Ag(2), and 4 Ca^{2+} ions at Ca(1) (see Figure 1). The remaining 45 % would have 2 Ag^+ ions at Ag(1) and 5 Ca^{2+} ions at Ca(1).

In this work, each Ag^+ ion at Ag(1) has moved relatively far into the large cavity, 1.399(4) Å from the (111) plane at 3 O(3)'s. Each Ca^{2+} ion at Ca(1) has moved ca. 0.801(7) Å into the large cavity, whereas each Ag^+ ion at Ag(2) is almost on the 6-ring plane of the unit cell, only recessed to

0.116(16) Å into the sodalite cavity from (111) plane of three O(3)'s (see Table III).

The Ag(1)-O(3) distance is 2.69(1) Å which is longer than the sum of the conventional ionic radii of Ag^+ and O^{2-} , 2.58 Å. This indicates that Ag(1)-O(3) bonds are relatively weak. The Ag(2)-O(3) distance is 2.30(2) Å which is less than the sum of the conventional ionic radii of Ag^+ and O^{2-} , 2.58 Å. This indicates that Ag(2)-O(3) bonds are quite covalent, as is usually found for Ag^+ in zeolite A²⁰. The geometry of Ag^+ at Ag(2) is near-trigonal planar (O(3)-Ag(2)-O(3)=119.8(6) Å (see Table II). In this structure, the Ca(1)-O(3) distance, ca. 2.43(1) Å, is somewhat longer than the sum of the conventional ionic radii of Ca^{2+} and O^{2-} , 2.31 Å¹² (see Table II). This distance shows that these bonds are relatively weak.

In this structure, 6.0 iodine molecules approach to the framework oxygen I(1)-O(1) distance, 3.42(2) Å is shorter than the nonbonded approach distance, 3.55 Å, calculated from the sum of the appropriate nonbonded van der Waals radii. The O(1)-I(1)-I(2) angle, 166.1(3)°, is nearly linear. Such an effect has been observed in complexes between diatomic

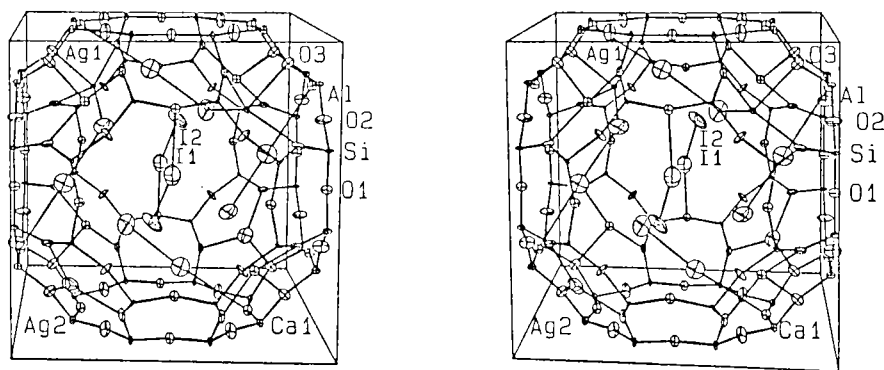


Fig 1. A stereoview of the large cavity of an iodine sorption complex of dehydrated $\text{Ag}_{3.1}\text{Ca}_{4.45}\text{-A}$. Two Ag^+ ions at Ag(1), two Ag^+ ions at Ag(2), four Ca^{2+} at Ca(1), and 6 iodine molecules are shown. About 55 % of unit cell may have this arrangement. Ellipsoids of 20 % probability are used.

halogen molecules and organic molecules.¹⁸⁾ This bonding can be understood in terms of charge transfer complexation, because the electronegative oxide ion at O(1) donates electron pair density toward axially electropositive region on the iodine molecule with its vacant 5p* antibonding molecular orbital.

The long diiodine bond, 2.92(2) Å, as compared to 2.662 Å in gas phase I₂,¹⁹⁾ is the consequence of the resulted reduced bond order due to the formation of this charge transfer complex. The Ag(1)-I(2) distance, 2.73(2) Å is much shorter than the sum of the conventional ionic radius of Ag⁺ and I⁻, 3.42 Å (see Table II). For comparison, Ag to I distance in AgI is 2.55 Å.

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

Atom			
O(2)	0.155(11) ^a	Ag(2)	-0.116(16)
Ag(1)	1.399(4)	Ca(1)	0.801(7)

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

In bromine sorption complexes of dehydrated Ag₃₁Ca₄₅-A, all cations do not interact with bromine molecules.²¹⁾ However, in the iodine sorption complex of Ag₃₁Ca₄₅-A, two Ag⁺ ions at Ag(1) approach and interact to the iodine molecules (see Figure 2).

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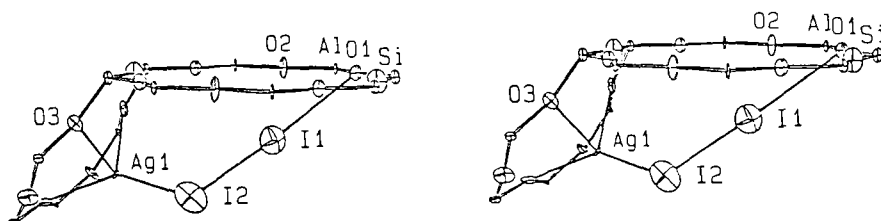


Fig 2. A stereoview of the structure about 8-ring. Each 8-ring oxygens participates in charge transfer interaction with a diiodine molecule approximately as shown. Ellipsoids of 10 % probability are used.

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