

칼슘 이온으로 완전히 치환된 제올라이트 A의 탈수 구조와 칼슘 치환 제올라이트 A에 요오드가 흡착된 착물 구조

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The Structures of Dehydrated Fully Ca²⁺-Exchanged Zeolite A and of Its Iodine Sorption Complex

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요 약

완전히 Ca²⁺ 이온으로 치환된 탈수구조(a=12.263(2) Å)와 이 결정에 요오드가 흡착된 구조(a=12.258(2) Å)를 21°C에서 입방공간군 Pm3m를 사용하여 단결정 X-선 회절법으로 구조를 해석하였다. 탈수구조는 I>3σ(I)인 206개의 반사를 사용하여 Rw값이 0.081까지 정밀화되었고 요오드가 흡착된 구조는 173개의 반사를 사용하여 Rw값이 0.084까지 정밀화되었다. 각각의 구조에서 단위세포당 6개의 Ca²⁺ 이온은 6-링의 산소와 결합하면서 3개의 다른 3회 회전축상에 위치하였다. 탈수한 칼슘 치환 제올라이트 A는 80°C에서 단위세포당 여섯개의 요오드 분자를 흡착하며 각 요오드 분자는 골조 산소 원자와 전하이동 착물을 형성하였다(I-O=3.32(3) Å, I-I=2.71(2) Å 그리고 I-I-O=180°).

Abstract

The structures of dehydrated fully Ca²⁺-exchanged zeolite A (a=12.263(2) Å) and of its iodine sorption complex (a=12.258(2) Å) have been determined by single-crystal X-ray diffraction methods in

the cubic space group, Pm3m at 21(1)°C. the structures were refined to final R(weighted) indices of 0.081 with 206 reflections and 0.084 with 173 reflections, respectively for which I>3σ(I). In each structure, six divalent cations are located on three different threefold axes associated with 6-ring oxygens. Dehydrated Ca²⁺-A sorbs ca. 6.0 diiodine molecules per unit cell at 80°C(vapor pressure of I₂ is ca. 14.3 Torr). Each iodine molecule makes a close approach, along its axis to framework oxygen atom with I-I distance of 2.71(2) Å, I-O distance of 3.32(3) Å, and I-I-O=180°. The result indicates that diiodine molecule forms charge transfer complex with framework oxygen.

INTRODUCTION

Synthetic zeolite 4A with stoichiometry of Na₁₂Al₁₂Si₁₂O₄₈·27H₂O per unit cell, is a crystalline aluminosilicate, well known for its industrial applications as an adsorbent, molecular sieve, and catalysts. 12 Na⁺ ions per unit cell of zeolite 4A may be easily exchanged. For example, when Na₁₂-A is exchanged with divalent cations, M²⁺, each divalent cation dis-

places two of the monovalent Na^+ cations. The ideal chemical composition of a unit cell is then $\text{Na}_{12-2x}\text{M}_x\text{Al}_{12}\text{Si}_{12}\text{O}_{48}\cdot n\text{H}_2\text{O}$ where x is the number of divalent cations introduced.^{1,2}

The exchangeable cations in zeolite A can occupy a site near the center of the 8-ring (α -site), that of the 6-ring (β -site), or that of 4-ring. The site selectivities of various cations have been extensively studied.^{1b} Takaishi and Ohgushi³ reported that one Ca^{2+} ion of $\text{Ca}_6\text{-A}$ occupies the 8-ring site and because of this 8-ring cation, $\text{Ca}_6\text{-A}$ is useful for an isomerization catalyst of 1-butene to 2-butene⁴. Firor and Seff also reported that five Ca^{2+} are located on threefold axes near the center of 6-oxygen ring and one Ca^{2+} ion is located in the plane of an 8-oxygen ring. However, Pluth and Smith reported that an 8-ring cation is not a Ca^{2+} ion but a K^+ ion due to the impurity from the solution for exchange.^{5,6}

The crystal structures of dehydrated $\text{Ca}_4\text{Na}_4\text{-A}$ ⁷ and of its diiodine sorption complex have been determined by the X-ray powder diffraction method with 85 and 65 independent reflections, respectively. In the dehydrated $\text{Ca}_4\text{Na}_4\text{-A}$ all 8 cations are associated with 6-ring oxygens; 4 Ca^{2+} ions are moved ca 0.22 Å into the large cavity from the (111) plane of the O(3) oxygens, and 4 Na^+ ions are displaced ca. 0.58 Å into the sodalite unit from the (111) plane of the O(3). In the iodine sorption structure of $\text{Ca}_4\text{Na}_4\text{-A}$, ca. 5.65 diiodine molecules are sorbed per unit cell. Each I_2 molecule make close approaches in its axial direction to a framework oxygen atom and to an iodine atom in an adjacent molecules, with an I-O distance of 3.29 Å and I-I distance of 3.46 Å.

Recently, the crystal structure of iodine sorption complexes of partially cobalt(II)-exchanged zeolite A, $\text{Co}_{3.5}\text{Na}_5\text{-A}$,⁸ have been determined. 3.5 Co^{2+} ions and 4.5 Na^+ ions occupied the 6-ring sites and 0.5 Na^+ occupied the 8-ring site. Therefore 2.5 eight-rings can accommodate 5 diiodine molecules, i.e., 2 I_2 per available 8-ring. Again each iodine molecule

makes a nearly linear approach (I-I-O = 175°), indicative of charge transfer complexation to an 8-ring oxygens.

In the crystal structure of a bromine sorption complex of zeolite 4A,⁹ six dibromine molecules were sorbed per unit cell and dibromine molecules appeared to interact neither with the anionic framework nor with the Na^+ ions.

In the crystal structures of chlorine sorption complexes of Eu(II)-exchanged zeolite A¹⁰ and Ag^+ -exchanged zeolite A,¹¹ chlorine gas is reported to oxidize Eu(II) to Eu(IV) and hexasilver to AgCl . In the latter structure, additional six dichlorine molecules are sorbed per unit cell: these form charge-transfer complexes with framework oxygens (O-Cl-Cl = 166(2)°).

This work was initiated to investigate the cation positions in the crystal structure of the dehydrated fully Ca^{2+} -exchanged zeolite A, to investigate iodine sorption by $\text{Ca}_6\text{-A}$ and to determine the positions of sorbed iodine molecules. By determining the number of sorbed iodine molecules associated with 8-ring oxygens, it was also hoped to verify further whether there is an Ca^{2+} ion in the plane of 8-oxygen ring or not.

EXPERIMENTAL SECTION

Crystals of zeolite 4A were prepared by Charnell's methods,¹² modified to include a second crystallization using seed crystals from the first synthesis. A single crystal about 0.085 mm on an edge was lodged in a fine glass capillary for each exchange. An exchange solution of 0.04325 M $\text{Ca}(\text{NO}_3)_2$ (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.

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 21(1)°C. Each crystal was placed in a finely drawn Pyrex capillary,

attached to a vacuum system and cautiously dehydrated by gradually increasing its temperature (ca. 25°/hr) to 350°C at a constant pressure of 2×10^{-6} Torr. Finally, the system was maintained at the state for 48 hours. After cooling to room temperature, the crystal, still under vacuum was sealed in its capillary by torch. The crystal was colorless.

To prepare the iodine complexes, the dehydrated $\text{Ca}_6\text{-A}$ crystal was treated with zeolitically dried I_2 vapor at 80°C (vapor pressure of I_2 was 14.3 Torr) for 24 hours. The resulting dehydrated crystal was initially deep blue but became black after exposure to iodine vapor. Finally, the crystal still in its iodine atmosphere was sealed in its capillary.

X-RAY DATA COLLECTION

The diffraction intensities were collected at 21(1)°C. The cubic space group Pm3m (no systematic absences) was used instead of Fm3c throughout this work for reasons discussed previously.^{13,14} Diffraction data were collected with an automated Enraf-Nonius Four circle computer controlled CAD-4 diffractometer, equipped with a graphite monochromator and a PDP micro 11/73 computer. Molybdenum radiation was used for all experiments ($\text{K}\alpha_1, \lambda=0.70930 \text{ \AA}$; $\text{K}\alpha_2, \lambda=0.71359 \text{ \AA}$). The unit cell constants were determined by least-squares refinements of 25 intense reflection for which $19^\circ < 2\theta < 24^\circ$ are $a=12.263(2) \text{ \AA}$ for $\text{Ca}_6\text{-A}$ (first crystal) and $a=12.258(2) \text{ \AA}$ for the iodine sorption complex of $\text{Ca}_6\text{-A}$ (second crystal), respectively.

For each crystal, reflections from two intensity-equivalent regions of reciprocal space ($hkl, h \leq k \leq l$ and $lkh, 1 \leq k \leq h$) were examined using the $\omega-2\theta$ scan technique. The data were collected using variable scan speed; 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 re-

gions 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 for each crystal were corrected for Lorentz and polarization effects; the reduced intensities were merged and the resultant estimated deviations were assigned to each average reflection by the computer programs, PAINT and WEIGHT.¹⁵

An absorption correction ($\mu\text{R}=0.03, \rho_{\text{cal}}=1.504 \text{ g/cm}^3$ and $F(000)=822$ for the first crystal, and $\mu\text{R}=0.23, \rho_{\text{cal}}=2.879 \text{ g/cm}^3$ and $F(000)=928$ for the second crystal) was judged to be negligible and was not applied.¹⁶ All unique reflections for which $2\theta < 70^\circ$ for both crystals were examined by counter methods. Only those for which $I > 3\sigma(I)$ were used for structure solution and refinement. These amounted to 206 of the 874 reflections examined for the dehydrated $\text{Ca}_6\text{-A}$, and 173 of the 874 reflections for the second crystal, respectively.

STRUCTURE DETERMINATION

Dehydrated $\text{Ca}_6\text{-A}$

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) of dehydrated $\text{Ag}_2\text{Ca}_5\text{-A}$.¹⁷ Anisotropic refinement of the framework atoms converged to an R_1 index, $(\sum |F_o - |F_c|| / \sum F_o)$ of 0.257 and a weighted R_2 index, $(\sum w(F_o - |F_c|)^2 / \sum wF_o^2)^{1/2}$ of 0.295. A subsequent difference Fourier function revealed two large peaks at (0.166, 0.166, 0.166) of height $6.64(2) \text{ e}\text{\AA}^{-3}$ and another at (0.210, 0.210, 0.210) of height of $4.47(2) \text{ e}\text{\AA}^{-3}$. Inclusion of these peaks as Ca(1) and Ca(2) lowered the error indices to $R_1=0.093$ and $R_2=0.097$ (see Table I). A difference Fourier function revealed a peak at (0.14, 0.14, 0.14) with a height of

2.21(2)eÅ⁻³. Simultaneous positional, thermal, and occupancy refinement including this position converged to R₁=0.070 and R₂=0.081.

The occupancy numbers of Ca²⁺ ions per unit cell were refined to Ca(1)=2.40(9), Ca(2)=2.47(9), and Ca(3)=1.04(8). These were fixed at Ca(1)=2.5, Ca(2)=2.5, and Ca(3)=1.0, respectively because the cationic charge should not be exceed +12 per Pm3m unit cell. The final R values were R₁=0.079 and R₂=0.081. The final difference function was featureless except an insignificant one at the origin of height 2.9(7) eÅ⁻³.

Iodine sorption complexes of the dehydrated Ca₆-A

Initial full-matrix least-squares refinement was in-

itiated using the atomic parameters of framework atoms from the previous Ca₆-A. Anisotropic refinement of the framework atoms converged to R₁=0.382 and R₂=0.401, respectively. From the initial difference Fourier function, I(1), I(2), and Ca(1) were readily located and refined (see Table I). Anisotropic refinement including these I(1), I(2) and Ca(1) positions, respectively, converged to R₁=0.229 and R₂=0.260.

A subsequent difference Fourier synthesis revealed two large peaks at(0.14,0.14,0.14) and (0.22,0.22,0.22) with a peak height of 2.77(3) eÅ⁻³ and 2.73(3) eÅ⁻³, respectively. These peaks were stable in least-squares refinement and lowered the error indices to R₁=0.091

Table 1. Positional, thermal, and occupancy parameters

(a) Crystal 1. (Dehydrated Ca₆-A)

Atom	Wyckoff Position	x	y	z	^b β ₁₁	^b β _{iso}
(Si,Al)	24(k)	0	1828(4)	3712(3)	35(2)	
O(1)	12(h)	0	2170(10)	5000	70(10)	
O(2)	12(i)	0	2854(9)	2854(9)	100(20)	
O(3)	24(m)	1123(4)	1123(4)	3205(5)	57(5)	
Ca(1)	8(g)	1708(9)	1708(9)	1708(9)	36(6)	
Ca(2)	8(g)	2080(10)	2080(10)	2080(10)	44(70)	
Ca(3)	8(g)	1400(20)	1400(20)	1400(20)	1.9(9) ^d	

β ₂₂	β ₃₃	β ₁₂	β ₁₃	β ₂₃	Occupancy	
					varied	fixed
21(2)	12(2)	0	0	9(5)		1.0 ^c
40(10)	40(10)	0	0	0		1.0
35(7)	35(7)	0	0	50(20)		1.0
57(5)	48(9)	30(20)	0(10)	0(10)		1.0
36(6)	36(6)	20(10)	20(10)	20(10)	0.300(10)	516
44(70)	44(70)	20(20)	20(10)	20(20)	0.309(11)	516
					0.130(10)	18

Table 1. Continued

(b) Crystal 2. (Iodine Soption Complex of the Dehydrated Ca₆-A)

Atom	Wyckoff Position	x	y	z	^b β ₁₁ ^b β _{iso}
(Si,Al)	24(k)	0	1829(6)	3715(5)	30(3)
O(1)	12(h)	0	2210(10)	5000	70(20)
O(2)	12(i)	0	2870(10)	2870(10)	100(20)
O(3)	24(m)	1089(8)	1089(8)	3380(10)	49(7)
Ca(1)	8(g)	1810(20)	1810(20)	1810(20)	41(9)
Ca(2)	8(g)	2170(10)	2170(10)	2170(10)	45(8)
Ca(3)	8(g)	1370(40)	1370(40)	1370(40)	3.3(17) ^d
I(1)	24(l)	1528(7)	4444(8)	5000	100(8)
I(2)	24(l)	2780(10)	3730(10)	5000	170(20)

β ₂₂	β ₃₃	β ₁₂	β ₁₃	β ₂₃	Occupancy	
					varied	fixed
19(3)	18(2)	0	0	17(9)		1.0 ^c
40(20)	30(10)	0	0	0		1.0
40(10)	40(10)	0	0	40(40)		1.0
49(7)	50(10)	80(20)	-10(20)	-10(20)		1.0
41(9)	41(9)	60(30)	60(30)	60(30)	0.228(10)	14
45(8)	45(8)	50(20)	50(20)	50(20)	0.355(10)	38
					0.141(11)	81
260(20)	230(10)	-150(20)	0	0	0.238(4)	14
260(20)	710(40)	70(40)	0	0	0.242(5)	14

^aPositional and anisotropic thermal parameters are given x 10⁴.

Numbers in parentheses are the esd's in the units of the least significant digit for the corresponding parameter.

^bThe anisotropic temperature factor = exp[-(β₁₁h² + β₂₂k² + β₃₃l² + β₁₂hk + β₁₃hl + β₂₃kl)].

Rms displacements can be calculated from β_{ij} values by using the formula, U_i = 0.225a(β_{ij})^{1/2}, where a = 12.263(2) Å for crystal 1 and a = 12.258(2) Å for crystal 2.

Occupancy for(Si)=1/2; occupancy for(Al)=1/2.

^cIstropic thermal parameter in units Å².

and R₂=0.077 (see Table I(b)).

The occupancy numbers at I(1) and I(2) refined to ca.5.7(1) and 5.8(1) iodine 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 diiodine molecules. The final R values were R₁=0.091 and R₂=

0.084. The largest peak on the final difference function was 1.6(8) eÅ⁻³ in height and was located at (0.0,0.0,0.0).

Atomic scattering factors for Ca²⁺, O⁻, I⁰, and (Si,Al)^{1.75+} were used^{18,19}. The function describing (Si,Al)^{1.75+} is the mean of the Si⁰, Si⁴⁺, Al⁰ and Al³⁺ function. All scattering factors were modified to account for anomalous dispersion correction^{20,21}. Final positional, thermal and occupancy parameters are pre-

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

	Crystal 1	Crystal 2
(Si,Al)-O(1)	1.635(6)	1.642(9)
(Si,Al)-O(2)	1.641(8)	1.64(1)
(Si,Al)-O(3)	1.676(5)	1.666(8)
Ca(1)-O(3)	2.28(1)	2.29(2)
Ca(2)-O(3)	2.31(1)	2.40(1)
Ca(3)-O(3)	2.46(2)	2.51(2)
I(1)-O(1)		3.32(3)
I(1)-O(2)		2.71(2)
O(1)-(Si,Al)-O(2)	114.9(6)	112.5(2)
O(1)-(Si,Al)-O(3)	112.5(4)	111.9(2)
O(2)-(Si,Al)-O(3)	103.9(3)	105.6(5)
O(3)-(Si,Al)-O(3)	108.4(4)	106.5(5)
(Si,Al)-O(1)-(Si,Al)	150(2)	147(2)
(Si,Al)-O(2)-(Si,Al)	169.8(6)	167.7(9)
(Si,Al)-O(3)-(Si,Al)	142.1(6)	144.3(9)
O(3)-Ca(1)-O(3)	118.0(3)	119.9(5)
O(3)-Ca(2)-O(3)	115.9(3)	120.4(3)
O(3)-Ca(3)-O(3)	105.4(3)	104(1)
O(1)-I(1)-I(2)		180(1)

sented in Table 1; bond angle and lengths are given in Table 2.

DISCUSSION

Dehydrated Ca₆-A

In this structure, 6 Ca²⁺ ions at Ca(1), Ca(2) and Ca(3) occupy 6-ring sites on the threefold axes of the unit cell (see Figure 1 and Table 1). The Ca²⁺ ions at Ca(1) and Ca(2) are 2.28(1) Å and 2.31(1) Å from their three nearest framework oxygens at O(3), respectively. For comparison, the sum of the conventional ionic radii of Ca²⁺ and O²⁻ is 2.31 Å.²² The Ca²⁺ ion at Ca(3) is 2.46(2) Å from its nearest neighbors, three O(3)'s.

2.5 Ca²⁺ ions at Ca(1) and 1 Ca²⁺ ion at Ca(3)

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

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

	Crystal 1	Crystal 2
O(2)	0.091(6)	0.135(9)
Ca(1)	-0.322(6)	-0.082(14)
Ca(2)	0.475(7)	0.677(9)
Ca(3)	-0.971(15)	-1.03(26)

are recessed 0.32 Å and 0.97 Å, respectively into the sodalite cavity from the (111) plane at O(3) (see Table III). 2.5 Ca²⁺ ions at Ca(2) are correspondingly recessed 0.47 Å into the large cavity.

In this structure, cations occupy only 6-ring sites; the 8-ring (and 4-ring) sites are empty. This occurs because the ionic radius of Ca²⁺ is relatively small. Larger cations such as Cs⁺, K⁺, and Tl⁺ preferentially occupy 8-ring sites.

During this work, another Ca²⁺ exchanged zeolite was prepared by using 0.1 M Ca(OH)₂ solution (Aldrich, 98.5%). The structure was determined and refined to R₁=0.065 and R₂=0.081 using 169 independent reflections for which I>3σ(I). This structure has ca. 0.6(1) K⁺ ions at the 8-ring site and ca. 5.8(2) Ca²⁺ ions at 6-ring sites. The K⁺ ions at the 8-ring site may be introduced from the impurity of the exchange solution.

The fractional occupancies observed at Ca(1) and Ca(2) indicate the existence of 2 types of unit cells in dehydrated Ca₆-A. About 50% of unit cell have 3 Ca²⁺ ions at Ca(1), 2 Ca²⁺ ions at Ca(2) and 1 Ca²⁺ ion at Ca(3). The remainder have 2 ions at Ca(1), ions at Ca(1) and 1 ion at Ca(3).

A plausible and unique relative arrangement of the six Ca²⁺ ions have been placed within their partially occupied equipoints so as to maximize the distribution of positive charge (to balance most evenly the anionic charge of the framework) and to minimize their electrostatic repulsions (by maximizing the shorter of their intercationic approaches). To minimize electrostatic repulsions, three Ca²⁺ ions at

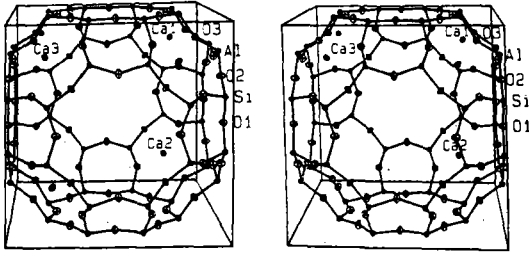


Fig 1. The unit cell of the dehydrated Ca_6-A is shown in stereoview. Six Ca^{2+} ions are distributed within their equipoints of partial occupancy in a plausible manner. About 50% of unit cells may have this arrangement. The remaining 50% would have 3 Ca^{2+} ions at Ca(1), 2 Ca^{2+} ions at Ca(2) and one Ca^{2+} ion at Ca(3). Ellipsoids of 20% probability are used.

Ca(2) are placed a triangular fashion(see figure 1).

Iodine Soption Complexes of the Dehydrated Ca_6-A .

In this structure, six Ca^{2+} ions occupy 6-ring sites on the threefold axes of the unit cell and no cation occupies 8-ring sites. Six diiodine molecules form charge transfer complexes with O(1) oxygens of 8-oxygen rings(see figures 2 and 3).

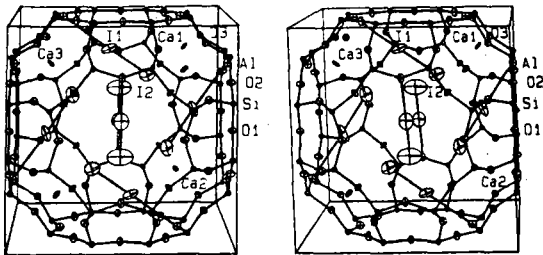


Fig 2. (b) The unit cell of iodine soption complexes of the dehydrated Ca_6-A is shown in stereoview. Two Ca^{2+} ions at Ca(1), three Ca^{2+} ions at Ca(2), one Ca^{2+} ion at Ca(3) and 6 diiodine molecules are shown, Ellipsoids of 20% probapility are used.

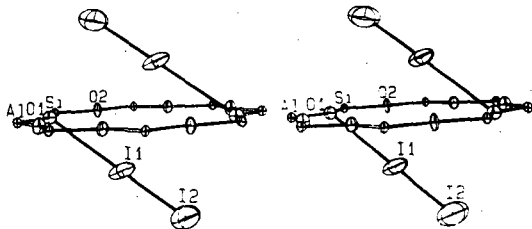


Fig 3. Each 8-oxygen ring in the structure participates in a charge transfer interaction with two diiodine molecules approximately as shown. Ellipsoids of 20% probability are used.

Diiodine molecule makes no significant approach to Ca^{2+} ions. In closest approach I- Ca^{2+} distance is 4.025(8) Å (see figure 2 and 3). The closest approach of the I(1) position to the framework atom is to O(1). Furthermore, the axis of the I_2 molecule points directly at an oxygen atom O(1). The O(1)-I(1)-I(2) angle, 180° is linear. Also the I(1)-O(1) distance, 3.32(3)Å is less than the sum of the appropriate nonbonded van der Waals radii, 3.55 Å.²³ This can be understood in terms of a degree of electron pair donation from the electronegative O(1) ion, the only crystallographic kind of oxygens not near a cation position, toward axially electropositive region on the iodine molecule with its vacant $5p\sigma^*$ antibonding molecular orbital.²⁴

The long diiodine bond, 2.71(2) Å, as compared to 2.662 Å in gas phase I_2^{25} are consequence of the resulted reduced bond order due to the formation of this charge transfer complex.

Iodine atoms are found to one quarter fill two 24-fold positions. These positions are interpreted to give 24 molecular sites which are occupied statistically by six I_2 molecules.

No more than six I_2 molecules can be accommodated at those positions. Otherwise, unreasonably short I-I distances, corresponding to overlapping molecules, would result.

Six Ca^{2+} ions are distributed over three nonequivalent threefold axis equipoints. Two Ca^{2+} ions at Ca(1) and one Ca^{2+} ion at Ca(3) are in the sodalite cavity 0.82 and 1.03 Å from the (111) plane at O(3), respectively. Three Ca^{2+} ions at Ca(II) extend 0.678 Å into the large cavity from the (111) plane of the oxygen 6-rings. The Ca^{2+} ions at Ca(1), Ca(2) and Ca(3) are trigonally coordinated to their respectively sets of three O(3) framework oxygens at 2.29(2), 2.40(1) and 2.51(2) Å, respectively.

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