Synthesis and Crystal Structure of Zinc Iodide in the Sodalite Cavities of Zeolite A (LTA)

Seok Han Kim,[a] Man Park,[b,*] Young Ja Son,[c] Hyung Joo Lee,[d] Gyo Cheol Jeong,[e] Myung Nam Bae,[f] and Woo Taik Lim[c,*]

[a]*Department of Applied Chemistry, Kyungpook National University, Daegu 702-701, Korea*
[b]*Department of Agricultural Chemistry, Kyungpook National University, Daegu 702-701, Korea*
[c]*Department of Applied Chemistry, Andong National University, Andong 760-749, Korea.* **E-mail: wtlim@andong.ac.kr*
[d]*Department of Electronics Engineering, Andong National University, Andong 760-749, Korea*
[e]*Department of Earth and Environmental Sciences, Andong National University, Andong 760-749, Korea*
[f]*Department of Chemistry, Pusan National University, Pusan 609-735, Korea*
Received November 23, 2006

The crystal structure of ZnI_2 molecule synthesized in zeolite A (LTA) has been studied by single-crystal X-ray diffraction techniques. A single crystal of $|Zn_6|[Si_{12}Al_{12}O_{48}]$-**LTA**, synthesized by the dynamic ion-exchange of $|Na_{12}|[Si_{12}Al_{12}O_{48}]$-**LTA** with aqueous 0.05 M $Zn(NO_3)_2$ and washed with deionized water, was placed in a stream of flowing 0.05 M KI in CH_3OH at 294 K for four days. The resulting crystal structure of the product $(|K_6Zn_3(KI)_3(ZnI_2)_{0.5}|[Si_{12}Al_{12}O_{48}]$-**LTA**, $a = 12.1690(10)$ Å) was determined at 294 K by single-crystal X-ray diffraction in the space group $Pm\bar{3}m$. It was refined with all measured reflections to the final error index $R_1 = 0.078$ for 431 reflections which $F_o > 4\sigma(F_o)$. At four crystallographically distinct positions, 3.5 Zn^{2+} and nine K^+ ions per unit cell are found: three Zn^{2+} and five K^+ ions lie on the 3-fold axes opposite 6-rings in the large cavity, two K^+ ions are off the plane of the 8-rings, two K^+ ions are recessed deeply off the plane of the 8-rings, and the remaining a half Zn^{2+} ion lie on the 3-fold axes opposite 6-rings in the sodalite cavity. A half Zn^{2+} ion and an I^- ion per unit cell are found in the sodalite units, indicating the formation of a ZnI_2 molecule in 50% of the sodalite cavities. Each ZnI_2 (Zn-I = 3.35(5) Å) is held in place by the coordination of its one Zn^{2+} ion to the zeolite framework oxygens and by the coordination of its two I^- ions to K^+ ions through 6-rings (I-K = 3.33(8) Å). Three additional I^- ions per unit cell are found opposite a 4-ring in the large cavity and form a K_3I^{2+} and two K_2ZnI^{3+} ionic clusters, respectively.

Key Words : Zeolite A, Zinc iodide, Single-crystal X-ray diffraction, Crystal structure

Introduction

Metal compound catalysts in solution or supported on solids, such as silica gel and zeolites, are used extensively.[1-6] Zeolites are one of the best supports for catalysts in the petro- and organo-chemical industries. Zeolites ion-exchanged by transition metal ions are also useful catalysts.[1,7] The catalytic properties of zeolites supported transition metal compounds have been studied intensively.[1] Various metal compounds and zeolites have been chosen to develop and control advanced catalytic reactions.[1] These catalytic reactions can be more easily controlled by using zeolites as support because the unique-sized metal compounds which are catalytically active materials, can be synthesized and stabilized in regular three-dimensionally arrayed cavities of zeolites. Additionally, the reactants and products can also be controlled due to the shape-selectivities of zeolites.[8]

Zinc halides, ZnX_2 (X = Cl, Br, I), are used as catalysts in various organic reactions. For cross-coupling reactions of carbonylmethyl units using α-chloroketones and tin enolates, zinc halides are used excellent catalysts.[9] One function of the ZnX_2 in the reactions is to serve as a Lewis acid promoting the precondensation step.[9] Polymer-supported zinc halides, $(PVP)ZnX_2$ (PVP = poly(4-vinylpyridine), X = Cl, Br, I), have also been reported as heterogeneous catalysts

with high selectivity and activity for the coupling reactions of carbon dioxide and epoxides.[2] $ZnCl_2$, ZnI_2, and $TiCl_4$ supported on silica gel are more efficient catalysts in various organic reactions,[3-5] such as the Friedel-Crafts alkylation of benzene with alkyl chlorides[3] and Diels-Alder reactions with different dienophiles[4,5] even though ZnX_2 and $TiCl_4$ are already good catalysts for these reactions.[3] The applicability of these materials in Diels-Alder reactions of furan is improved by supporting it on silica gel.[3] Additionally, silica gel-supported ZnX_2 catalysts also provide an efficient synthesis of aryl-substituted halo olefins from aromatic ketones and acetyl halides with the some advantages of operational simplicity, mild conditions, high yield, and stereoselectivity.[6]

Group II*b* iodides, ZnI_2, CdI_2, and HgI_2, have been studied for their optical properties.[10,11] Specifically, HgI_2 has been studied because of its optical properties and its utility as radiation detector and CdI_2 has also been extensively researched due to its polytypism.[10,11] In recent decades, the optical and structural properties of ZnI_2 films have also been studied using optical-absorption measurement.[10,11] The optical band gap of ZnI_2 films is the direct-type and shows thickness dependence related packing density and size distribution of crystallite grains.[10,11] A large decrease in band gap has been attributed to the large c/a and this result indicates the optical

properties of group II*b* iodides are changed by their crystal structures.[10,11]

In this work, we have attempted to synthesize ZnI_2 clusters in a single crystal of zeolite A and to determine its structure. This was done because the ZnI_2 clusters in the unique-sized and regular three-dimensionally orientated cavities of zeolites are predicted to be advanced catalytic and optical materials. The resulting crystal, $|K_6Zn_3(KI)_3(ZnI_2)_{0.5}|[Si_{12}Al_{12}O_{48}]$-**LTA** including ZnI_2 molecules, was prepared through a reaction of KI in CH_3OH solution with the fully Zn^{2+}-exchanged zeolite A ($|Zn_6|[Si_{12}Al_{12}O_{48}]$-**LTA**). The crystal structure of the resulting product was determined to verify that nanoclusters had formed, to learn their positions, size, and geometry, and to observe their interactions with zeolite framework. The method used closely parallel those reported earlier for $|K_9(K_4I)(Ag_4I_4)_{0.5}|[Si_{12}Al_{12}O_{48}]$-**LTA**,[12] $|K_9(K_4Br)$- $(Ag_4Br_4)_{0.75}|[Si_{12}Al_{12}O_{48}]$-**LTA**,[13] and $|K_6(Pb_4I_2)(PbI_2)_{0.67}(H_2O)_2|$- $[Si_{12}Al_{12}O_{48}]$-**LTA**.[14]

Experimental Section

Large colorless single crystals of zeolite 4A ($|Na_{12}(H_2O)_{27}|$-$[Si_{12}Al_{12}O_{48}]$-**LTA**, Na$_{12}$-A, or Na-A) were synthesized by Kokotailo and Charnell.[15] These crystals were from the same batch as all previous zeolite A single crystals reported from K. Seff's and N. H. Heo's laboratories.[12-14] A colorless single crystal of hydrated Na-A, a cube about 80 μm on an edge, was lodged in a fine Pyrex capillary. Crystals of hydrated $|Zn_6|[Si_{12}Al_{12}O_{48}]$-**LTA** were prepared using the dynamic (flow) ion-exchange of $|Na_{12}(H_2O)_{27}|[Si_{12}Al_{12}O_{48}]$-**LTA** with aqueous 0.05 M $Zn(NO_3)_2$ (Aldrich 99.999%) at 294 K for 4 days.[16] The resulting $|Zn_6|[Si_{12}Al_{12}O_{48}]$-**LTA** crystal was thoroughly washed with deionized water and then placed in a flowing stream of 0.05 M KI (Aldrich 99.99%) in CH_3OH (Merck 99.8%) at 294 K for 4 days. No attempt was made to dry the CH_3OH beforehand. At the end, no attempt was made to remove the solvent from the crystal, neither by evacuation nor heating. The crystal was then isolated in its capillary by sealing both ends with a small torch. After ion-exchange with Zn^{2+} and a consecutive reaction with KI, the crystal was colorless.

X-ray diffraction data of the single-crystal was collected at 294(1) K on an ADSC Quantum210 detector at Beamline 4A MXW of The Pohang Light Source. The wavelength of the synchrotron X-rays was 0.76999 Å. The crystal was rotated through a total of 360°, with a 1.0° oscillation per frame. We got basic scale file from program the HKL2000 (Otwinowski & Minor, 1997) program which included the DENZO indexing program with the cubic space group *P23*. A full-matrix least-squares refinement using SHELEX97[17] with the cubic space group *Pm$\bar{3}$m* (no systematic absences) was carried out on this work for reasons discussed previously.[16-20] A summary of the experimental and crystallographic data is presented in Table 1.

Structure Determination

Table 1. Summary of Experimental and Crystallographic Data

Crystal cross-section (mm)	0.08
Ion exchange for Zn^{2+} (days, mL)	4, 8
Washing with deionized water (K, day)	294, 1
Reaction of Zn-A with KI (days, mL)	4, 12
Temperature for data collection (K)	294(1)
X-ray source	PLS(4A MXW BL)[a]
Wavelength (Å)	0.76999
Space group, No.	Pm$\bar{3}$m, 221
Unit cell constant, a (Å)	12.1690(10)
Maximum 2θ for data collection (deg)	61.93
No. of unique reflections measured, m	483
No. of reflections ($F_o > 4\sigma(F_o)$)	431
No. of variables, s	48
Data/parameter ratio, m/s	10.1
Weighting parameters : a/b	0.130/8.660
Final error indices	
$R_1{}^b$	0.078
$R_2{}^c$	0.215
Goodness of fit^d	1.118

[a]Beamline 4A MXW of Pohang Light Source. [b]$R_1 = \Sigma|F_o - |F_c||/\Sigma F_o$; R_1 is calculated using only the 431 reflections for which $F_o > 4\sigma(F_o)$. [c]$R_2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$; R_2 is calculated using all 483 unique reflections measured. [d]Goodness-of-fit $= (\Sigma w(F_o{}^2 - F_c{}^2)^2/(m - s))^{1/2}$.

A full-matrix least-squares refinement using SHELXL97[17] was done on $F_o{}^2$ using all reflections. This began with the atomic parameters of the framework atoms [(Si,Al), O(1), O(2), and O(3)] (see Table 2) in dehydrated $|K_{12}|[Si_{12}Al_{12}O_{48}]$-**LTA**.[21] The initial refinement using isotropic thermal parameters for all positions converged to the error indices (defined in footnotes to Table 1) $R_1 = 0.44$ and $R_2 = 0.78$.

See Table 3 for the steps of structure determination and refinement as new atomic positions were found on successive difference Fourier electron-density functions. The refinement with ten additional peaks from Fourier difference functions and isotropic thermal parameters to refine the framework atoms led to convergence with $R_1 = 0.11$ and $R_2 = 0.32$. These framework atoms and some atoms opposite 6-ring were allowed to refine anisotropically (see Table 2) and the refinement converged to $R_1 = 0.078$ and $R_2 = 0.208$. The final cycles of the refinement were carried out with occupancies fixed at the values given in Tables 2 and 3. This model converged to the final error indices $R_1 = 0.078$ and $R_2 = 0.215$. In the last cycle of least-squares refinement, all shifts were less than 0.1% of their corresponding estimated standard deviations. Final structural parameters are presented in Table 2 and selected interatomic distances and angles are given in Table 4.

Fixed weights were used initially; the final weights were assigned using the formula $w = 1/[\sigma^2(F_o{}^2) + (aP)^2 + bP]$ where $P = [Max(F_o{}^2, 0) + 2F_c{}^2]/3$, with $a = 0.130$ and $b = 8.660$ as refined parameters (see Table 1). Atomic scattering factors for Zn^{2+}, I^-, K^+, O^-, and $(Si,Al)^{1.75+}$ were used.[22,23] The function describing $(Si,Al)^{1.75+}$ is the mean of the Si^{4+}, Si^0, Al^{3+}, and Al^0 functions. All scattering factors were

Table 2. Positional, Thermal, and Occupancy Parameters[a]

	Wyckoff position	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	Occupancy[b]	
											fixed	varied
(Si,Al)	24(k)	0	1830(1)	3686(1)	68(10)	21(10)	0(10)	0	0	12(5)	24[c]	
O(1)	12(h)	0	2126(7)	5000[d]	1601(121)	409(47)	201(38)	0	0	0	12	
O(2)	12(i)	0	2991(4)	2991(4)	449(39)	232(20)	232(20)	0	0	56(25)	12	
O(3)	24(m)	1137(5)	1137(5)	3308(7)	512(25)	512(25)	840(47)	253(29)	−288(28)	−288(28)	24	
Zn(1)	8(g)	1623(21)	1623(21)	1623(21)	335(52)	335(52)	335(52)	102(85)	102(85)	102(85)	0.5	0.4(2)
Zn(2)	8(g)	1947(10)	1947(10)	1947(10)	114(28)						1	1.2(2)
Zn(3)	8(g)	2160(5)	2160(5)	2160(5)	156(14)						2	2.0(2)
K(1)	8(g)	2544(6)	2544(6)	2544(6)	378(18)	378(18)	378(18)	116(27)	116(27)	116(27)	3	3.2(3)
K(2)	8(g)	3022(17)	3022(17)	3022(17)	1131(84)						2	1.9(2)
K(3)	24(m)	326(46)	4589(25)	4589(25)	1462(260)						2	3.2(5)
K(4)	24(l)	1067(54)	4274(51)	5000[d]	1584(274)						2	2.3(6)
I(1)	8(g)	964(39)	964(39)	964(39)	4702(528)						1	1.1(1)
I(2)	24(m)	3115(55)	3115(55)	4442(66)	5832(648)						2	2.8(4)
I(3)	24(l)	2087(34)	3471(33)	5000[d]	1347(113)						1	0.8(2)

[a]Positional parameters $\times 10^4$ and thermal parameters $\times 10^4$ are given. Numbers in parentheses are the estimated standard deviations in the units of the least significant figure given for the corresponding parameter. The anisotropic temperature factor is $\exp[-2\pi^2 a^{-2}(U_{11}h^2 + U_{22}k^2 + U_{33}l^2 + 2U_{12}hk + 2U_{13}hl + 2U_{23}kl)]$. [b]Occupancy factors are given as the number of atoms or ions per unit cell. [c]Occupancy for (Si) = 12, occupancy for (Al) = 12. [d]Exactly 0.5 by symmetry.

Table 3. Steps of Structure Determination as Atom Positions Are Found

step/ atom	occupancies per unit cell										error indices[f]	
	Zn(1)	Zn(2)	Zn(3)	K(1)	K(2)	K(3)	K(4)	I(1)	I(2)	I(3)	R_1	R_2
1[a]											0.435	0.780
2				5.1(4)							0.253	0.673
3			2.3(1)	2.5(3)							0.205	0.564
4	0.8(2)		1.9(2)	2.7(3)							0.172	0.534
5	0.6(1)	1.1(2)	2.1(2)	2.7(2)							0.166	0.503
6	0.6(1)	1.1(2)	2.1(2)	2.7(2)	2.3(4)						0.156	0.462
7	0.7(1)	1.1(2)	2.0(2)	2.5(2)	2.3(3)			1.4(4)			0.147	0.455
8	0.5(1)	1.4(2)	1.9(2)	2.3(2)	2.1(3)	1.6(5)		1.2(3)			0.136	0.350
9	0.5(1)	1.5(2)	1.8(2)	2.4(2)	2.4(3)	2.7(5)	3.4(6)	1.2(3)			0.122	0.322
10	0.5(1)	1.5(2)	1.8(2)	2.4(2)	2.4(3)	2.2(5)	2.1(9)	1.2(3)		1.0(2)	0.119	0.318
11	0.5(1)	1.5(2)	1.9(2)	2.6(2)	2.5(4)	4.3(6)	1.7(9)	1.2(2)	2.5(6)	0.8(2)	0.114	0.317
12[b]	0.4(1)	1.5(2)	1.8(1)	2.7(1)	1.9(2)	3.2(5)	2.3(6)	1.1(1)	2.8(4)	0.8(4)	0.0786	0.210
13[c]	0.4(2)	1.2(2)	2.0(2)	3.2(3)	1.9(2)	3.2(5)	2.3(6)	1.1(1)	2.8(4)	0.8(2)	0.0777	0.208
14[c,d]	0.5	1.0	2.0	3.0	2.0	2.0	2.0	1.0	2.0	1.0	0.0783	0.215

[a]The initial step of structure determination as all framework atoms are found. [b]Framework atoms were allowed to refine anisotropically. [c]Framework atoms and some atoms opposite six-ring were allowed to refine anisotropically (see Table 2). [d]Fixed occupancies are used for all atoms. [f]Defined in footnotes to Table 2.

modified to account for anomalous dispersion.[24,25]

Results and Discussion

Zeolite A Framework and Cations. The flex of (distortion to) the framework structure of the zeolite |K_6Zn_3(KI)_3-(ZnI_2)_0.5|[Si_12Al_12O_48]-**LTA** is much more like that of hydrated |Zn_6|[Si_12Al_12O_48]-**LTA** and evacuated |K_2Zn_5|[Si_12Al_12O_48]-**LTA** than that of evacuated |Zn_6|[Si_12Al_12O_48]-**LTA**, dehydrated |K_12|[Si_12Al_12O_48]-**LTA**, and hydrated |K_12|[Si_12Al_12O_48]-**LTA** (see Table 5).[16,20,21]

In each unit cell of the zeolite |K_6Zn_3(KI)_3(ZnI_2)_0.5|-[Si_12Al_12O_48]-**LTA**, three and a half Zn^{2+} and nine K^+ ions are distributed over four crystallographically distinct positions; on the 3-fold axes opposite 6-ring, a half, one, and two Zn^{2+} ions are found at Zn(1), Zn(2), and Zn(3), respectively, and three and two K^+ ions at K(1) and K(2), respectively, are also found. Additionally, two K^+ ions at K(3) are found on near 8-rings and two K^+ ions at K(4) lie on deeply off the plane of the 8-rings in the large cavities. Therefore, the eight 6-rings per unit cell contain three and a half Zn^{2+} and five K^+ ions; each Zn^{2+} and K^+ ion lies on a 3-fold axis and those ions at Zn(1), Zn(2), Zn(3), K(1), and K(2) extend 0.50, 0.18, 0.63, 1.44, and 2.45 Å, respectively, from the (111) planes at O(3) (see Table 6).

The Zn^{2+} ions at Zn(1) in the sodalite units, and at Zn(2)

Table 4. Selected Interatomic Distances (Å) and Angles (deg)[a]

	Distances		Angles
(Si,Al)-O(1)	1.639(3)	O(1)-(Si,Al)-O(2)	108.2(4)
(Si,Al)-O(2)	1.647(2)	O(1)-(Si,Al)-O(3)	112.1(3)
(Si,Al)-O(3)	1.684(3)	O(2)-(Si,Al)-O(3)	106.8(3)
		O(3)-(Si,Al)-O(3)	110.5(5)
Zn(1)-O(3)	2.215(14)		
Zn(2)-O(3)	2.165(10)	(Si,Al)-O(1)-(Si,Al)	154.6(6)
Zn(3)-O(3)	2.248(10)	(Si,Al)-O(2)-(Si,Al)	151.8(5)
K(1)-O(3)	2.594(11)	(Si,Al)-O(3)-(Si,Al)	138.4(6)
K(2)-O(3)	3.26(3)		
K(3)-O(2)	2.78(5)	O(3)-Zn(1)-O(3)	115.1(9)
K(4)-O(1)	2.92(6)	O(3)-Zn(2)-O(3)	119.3(2)
		O(3)-Zn(3)-O(3)	112.4(3)
Zn(1)-I(1)	3.35(5)	O(3)-K(1)-O(3)	92.2(4)
K(1)-I(1)	3.33(8)	O(3)-K(2)-O(3)	69.9(7)
Zn(3)-I(2)	3.23(9)		
K(2)-I(2)	3.09(9)	I(1)-Zn(1)-I(1)	59.5(21)
K(4)-I(2)	3.39(5)	O(3)-Zn(1)-I(1)	84.6(12)/138.0(17)
K(1)-I(3)	3.243(18)	Zn(3)-I(2)-K(2)	146(3)
K(3)-I(3)	3.23(6)	Zn(3)-I(2)-K(4)	85.8(16)
		K(2)-I(2)-K(4)	93.3(14)
Zn(1)⋯K(2)	2.945(6)	K(1)-I(3)-K(1)	134.4(14)
Zn(1)⋯I(1)	1.39(8)	K(1)-I(3)-K(3)	103.0(7)/120.8(10)
I(1)⋯I(1)	3.32(13)		
I(1)⋯O(3)	2.87(5)		
I(2)⋯O(3)	3.67(10)		
I(3)⋯O(1)	3.02(4)		

[a]The numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding parameters.

and Zn(3) in the large cavities are 2.215(14), 2.165(10), and 2.248(10) Å, respectively, away from three O(3) oxygens. The approach distance from the Zn^{2+} ions on the 3-fold axis to O(3), Zn(1)-O(3) = 2.215(14) Å, Zn(2)-O(3) = 2.165(10) Å, and Zn(3)-O(3) = 2.248(10) Å, are reasonable considering the distances of Zn^{2+} to the framework oxygen that were found in previous works (1.99 Å to 2.30 Å)[16,20] and the sum of ionic radii of Zn^{2+} and O^{2-}, γ_{Zn}^{2+} (0.74 Å) + γ_O^{2-} (1.32 Å) = 2.06 Å[26] with their esds.

K^+ ions at K(1) and K(2) are 2.584(11) Å and 3.26(3) Å, respectively, from three O(3) oxygens of a 6-ring (see Table 4). The K(1)-O(3) distance, 2.584(11) Å, is similar to the sum of the ionic radii of K^+ and O^{2-}, 1.33 Å + 1.32 Å = 2.65 Å[26] but the K(2)-O(3) distance, 3.26(3) Å, is much longer than the sum.[26] Such somewhat longer approach distances from framework oxygens can be explained by all of K^+ ions at K(2) making clusters with I^- ions or H_2O molecules in the large cavities (*vide infra*). These longer distances of K^+ ions are also observed in dehydrated $|K_{12}|[Si_{12}Al_{12}O_{48}]$-**LTA** and hydrated $|K_{12}|[Si_{12}Al_{12}O_{48}]$-**LTA**.[21] The K^+ ions at K(1) and K(2) extend 1.44 Å and 2.45 Å, respectively, into the large cavity from the (111) planes at O(3) (see Table 5), and make different angles with O(3), O(3)-K(1)-O(3) = 92.2(4)° and O(3)-K(2)-O(3) = 69.9(7)°. Additionally, the K(1)-O(3) distance, 2.584(11) Å, is very close to the calculated K-O distance, 2.65 Å,[26] because two thirds of the K^+ ions at K(1) bond to I^- ions at I(1) in the sodalite cavities and also bond to I^- ions at I(3) in the large cavities with their reasonable

Table 5. (Si,Al)-O-(Si,Al) Angles (deg)[a] at Framework Oxygens and Unit Cell Parameters for K^+- and Zn^{2+}-exchanged Zeolite A

Zeolites	O(1)	O(2)	O(3)	a, Å
Dehydrated $|K_{12}|[Si_{12}Al_{12}O_{48}]$-**LTA**[b]	128.5(6)	178.4(5)	153.7(5)	12.309(2)
Hydrated $|K_{12}|[Si_{12}Al_{12}O_{48}]$-**LTA**[b]	145.2(9)	159.3(6)	146.0(9)	12.301(2)
Evacuated $|Zn_6|[Si_{12}Al_{12}O_{48}]$-**LTA**[c]	176.3(5)	144.9(6)	130.5(4)	12.049(1)
Hydrated $|Zn_6|[Si_{12}Al_{12}O_{48}]$-**LTA**[c]	160.0(8)	150.0(9)	139.5(7)	12.163(1)
Evacuated $|K_2Zn_5|[Si_{12}Al_{12}O_{48}]$-**LTA**[d]	156.1(10)	149.4(7)	136.7(6)	12.075(2)
$|K_6Zn_3(KI)_3(ZnI_2)_{0.5}(H_2O)_x|[Si_{12}Al_{12}O_{48}]$-**LTA**[e]	154.6(6)	151.8(5)	138.4(6)	12.169(1)

[a]The numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding parameters. [b]Reference 21. [c]Reference 16. [d]Reference 20. [e]This work.

Table 6. Deviations of Atoms (Å) from the (111) Plane at O(3)[a]

	$|K_6Zn_3(KI)_3(ZnI_2)_{0.5}|$-**LTA**[b]	Evacuated $|K_2Zn_5|$-**LTA**[c]	Dehydrated $|Zn_6|$-**LTA**[d]	Hydrated $|Zn_6|$-**LTA**[d]	Dehydrated $|K_{12}|$-**LTA**[e]	Hydrated $|K_{12}|$-**LTA**[e]
Zn(1)	−0.50	−0.59	−0.64	−3.86		
Zn(2)	0.18	0.20	0.16	0.66		
Zn(3)	0.63	0.91				
K(1)	1.44				0.79	1.49
K(2)	2.45					
K(3)					3.45	5.26
K(4)					−1.35	
K(5)					−0.19	
I(1)	−1.89					
O(4)		−2.76	−1.93			3.34
O(5)		2.92	2.63			−1.94

[a]A positive deviation indicates that the ion lies in the large cavity. A negative deviation indicates that the ion lies on the same side of the plane as the origin, *i.e.*, inside the sodalite unit. [b]This work. [c]Reference 20. [d]Reference 16. [e]Reference 21.

distances and structure (*vide infra*).

Per unit cell, two K^+ ions at K(3) are found on near 8-rings and two K^+ ions at K(4) are also found on deeply off the plane of the 8-rings in the large cavities. The K^+ ions at K(3) and K(4) are 2.78(5) Å and 2.92(6) Å from framework oxygen at O(2) and O(1), respectively. The approach distance is somewhat longer than the calculated one, 2.65 Å, but the longer distances of 8-ring cations from the framework oxygen are observed in many monopositive cationic forms of zeolite A. The two kinds of crystallographic positions and somewhat longer distances of 8-ring cations can be explained by existence of two kinds of K^+-included clusters near 8-rings in the large cavities (*vide infra*).

Including all of the cationic ions that are found, the total charge of the unit cell is +3.34 ((3.5 × (+2)) + (9.0 × (+1)) − 12 = +16.0). This is because occupancies of all of Zn^{2+} and K^+ ions per unit cell are 3.5 and 9, respectively, and the charge of framework per unit cell is −12. Therefore, some additional negative ions are needed in the unit cell to make neutral charged unit cells. This is shown in Tables 2 and 3.

ZnI_2 Molecule in the Sodalite Unit. In the sodalite units, 0.5 Zn^{2+} ions and one I^- ion per unit cell occupy nonequivalent 3-fold axes positions, indicating a ZnI_2 molecule is formed in 50% of the sodalite units. The 0.5 Zn^{2+} ions at Zn(1) lie opposite a 6-ring in the sodalite unit and the one I^- ion at I(1) occupies a similar positions, recessed more deeply into the sodalite unit. It is impossible for both a Zn^{2+} and a I^- ion to approach the same 6-ring because their approach distance, 1.39(8) Å, would be too short.

Each Zn^{2+} ion at Zn(1) is 2.215(14) Å from three O(3) oxygens of a 6-ring (see Table 4) and extend 0.50 Å into the sodalite unit from the (111) planes at O(3) (see Table 6). The Zn(1)-O(3) distance, 2.215(14) Å, is similar to those were found in previous works (1.99 Å to 2.30 Å)[16,20] and indicate the ion at Zn(1) are Zn^{2+} ions.

The occupancy of I^- ion at I(1), 1.0, is equal to twice of that of Zn^{2+} ions at Zn(1), 0.5, and extend 1.89 Å into the sodalite unit from the (111) planes at O(3) (see Table 6). They are thus far from the three nearest anionic framework oxygens, indicating that they are not cations. Furthermore, the bonding distance of I(1) to the nearest Zn^{2+} ion at Zn(1), 3.35(5) Å, is somewhat longer than the sum of ionic radii of Zn^{2+} and I^-, γ_{Zn}^{2+} (0.74 Å) + γ_I^- (2.16 Å) = 2.90 Å.[26] The I^- ions at I(1) lie on the other side of 6-rings that are occupied with K^+ ions at K(1) in the large cavities and can bond to K^+ ions at K(1) opposite adjacent 6-rings (K(1)-I(1) = 3.33(8) Å). Considering the sum of ionic radii between K^+ and I^-, γ_{K}^+ (1.33 Å) + γ_I^- (2.16 Å) = 3.49 Å,[26] and its esd, the K(1)-I(1) distances are reasonable.

Considering the occupancies of Zn^{2+} ions at Zn(1) and I^- ion at I(1), 0.5 and 1.0, respectively, (see Table 2) and the possible arrangements of Zn^{2+} and I^- ions within the space of the sodalite unit, one ZnI_2 molecule in the 50% of the sodalite units is most likely (see Figures 1, 2, and 3). In this arrangement, one Zn^{2+} ion bonds to two I^- ions (in addition to three framework oxygens), and each I^- ion bonds to one Zn^{2+} ion (in addition to one K^+ ion at K(1)). The stereoview
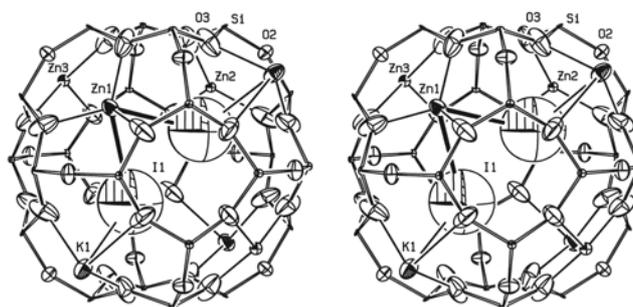
Figure 1. A stereoview of a sodalite cavity in $|K_6Zn_3(KI)_3(ZnI_2)_{0.5}|$-$[Si_{12}Al_{12}O_{48}]$-**LTA** containing a ZnI_2 molecule. 50% of the sodalite cavities contain a ZnI_2 molecule (heavy lines) as shown. One Zn^{2+} at Zn(1) coordinate to three O(3) oxygens. The zeolite A framework is drawn with bonds of medium thickness between oxygens and tetrahedrally coordinated (Si,Al) atoms. The coordinations of K^+ and Zn^{2+} ions to oxygens of zeolite framework are indicated by the thinnest lines. Ellipsoids of 20% probability are shown.
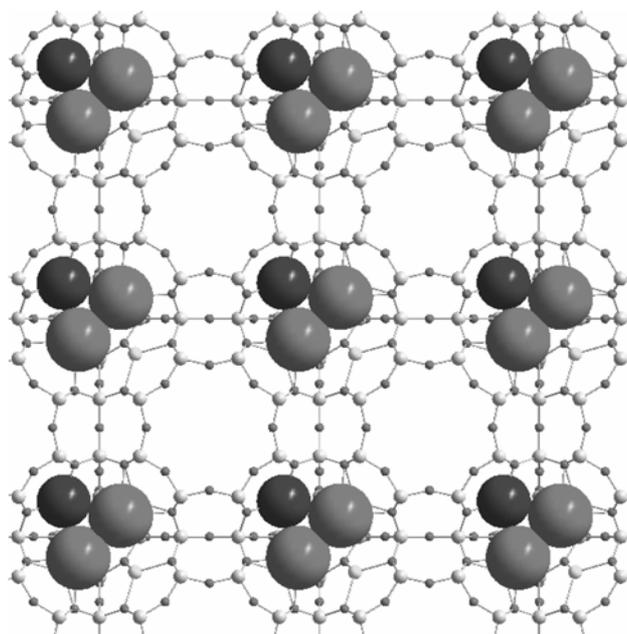
Figure 2. Two dimensional diagram of framework, building units, cavities, and location ZnI_2 molecules in sodalite cavities of several unit cells. For clarity, the framework atoms and cations have been simplified. The long-range ordering and identical orientations of the nanoparticles shown here is reasonable, but it has not been established in this work.

of such a sodalite unit with a ZnI_2 molecule is shown in Figure 1.

The ZnI_2 molecules in the sodalite cavities of this crystal are likely to be very stable because the absorbed and captured molecules within nano-sized spaces are highly resistant to high temperature and sudden changes in temperature and vacuum conditions. Additionally, this synthesis method, dynamic ion-exchange with aqueous solutions at room temperature, has been extensively used to make various other nanoclusters, Ag_4I_4,[12] Ag_4Br_4,[13] and PbI_2,[14] in the sodalite cavities because it is more productive and efficient compared to other methods such as thermal diffusion with
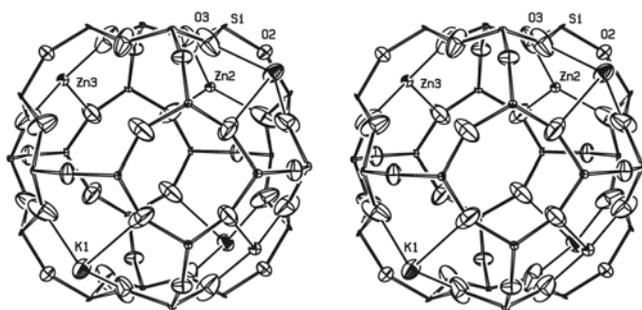
Figure 3. A stereoview of a sodalite cavity in $|K_6Zn_3(KI)_3(ZnI_2)_{0.5}|$-$[Si_{12}Al_{12}O_{48}]$-**LTA** without containing any ZnI_2 molecule. See the caption to Figure 1 for other details.
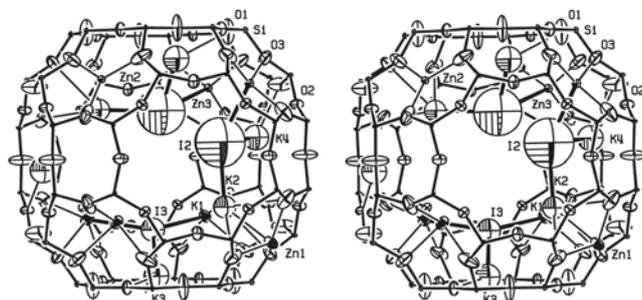
Figure 4. Stereoview of the large cavity of $|K_6Zn_3(KI)_3(ZnI_2)_{0.5}|$-$[Si_{12}Al_{12}O_{48}]$-**LTA** with Zn^{2+} at Zn(1). Two K_2ZnI^{3+} and a K_3I^{2+} ionic clusters are shown in this figure. Heavy lines indicate K^+-I^- and Zn^{2+}-I^- bonds. See the caption to Figure 1 for other details.

vapor.

Zn-K-I Clusters in the Large Cavities. Three I^- ions per unit cell are found opposite 4-rings in the large cavity; two at I(2) and one at I(3) per unit cell are opposite 4-ring in the large cavities, respectively, but the I^- ions at I(2) and I(3) are found at two different positions (see Table 2). Therefore, two kinds of clusters with an I^- ion at I(2) or I(3) are predicted: two clusters with an I^- ion at I(2) and another with an I^- ion at I(3).

Two K_2ZnI^{3+} cluster per unit cell are found in the large cavities and each of those includes an I^- ion at I(2). Each K_2ZnI^{3+} cluster consists of two K^+ ions (one at K(2) and one at K(4)), a Zn^{2+} ion at Zn(3), and an I^- ion at I(2) and has a trigonal plane form with its center at I(2) (see Figures 4 and 5). The approach distances of K(2)-I(2), K(4)-I(2), and Zn(3)-I(2) are 3.09(9), 3.39(5), and 3.23(9) Å, respectively. The distances are reasonable with esds as compared with the calculated distance of 3.49 and 2.90 Å for Zn-I and K-I, respectively. The angles are also reasonable with a possible geometry of the moiety, too (K(2)-I(2)-Zn(3) = 146(3)^o, K(4)-I(2)-Zn(3) = 85.8(16)^o, and K(2)-I(2)-K(4) = 93.3(14)^o). Additionally, the somewhat long distance of K(2)-O(3), 3.26(3) Å (*vide supra*), can be explained by each of K^+ ions at K(2) making ionic bonds with an I^- ion at I(2) in a K_2ZnI^{3+} cluster.

The other iodide ion per unit cell is found at I(3), opposite a 4-ring in the large cavity. It bonds to three K^+ ions (two at K(1) and one at K(3)) in a trigonal plane manner to give a
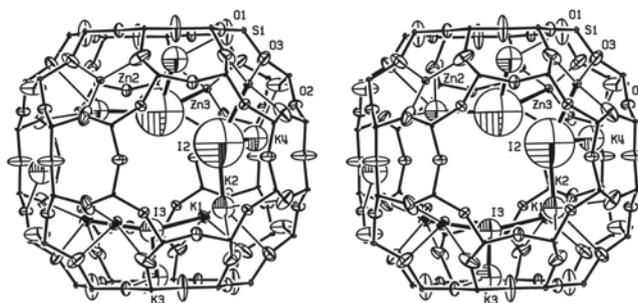
Figure 5. Stereoview of the large cavity of $|K_6Zn_3(KI)_3(ZnI_2)_{0.5}|$-$[Si_{12}Al_{12}O_{48}]$-**LTA** without Zn^{2+} at Zn(1). See the caption to Figures 1 and 3 for other details.

K_3I^{2+} cluster (see Figures 4 and 5). The bonding distances of K(1)-I(3) and K(3)-I(3) are 3.243(18) and 3.23(6) Å, respectively. These are close to the sum of K-I ionic radii, 3.49 Å,[26] considering their esds. The angle of K(1)-I(3)-K(1) is 134.4(14)^o and those of K(1)-I(3)-K(3) are 103.0(7)^o and 120.8(10)^o. Furthermore, the sum of these angles of the K_3I^{2+} cluster is near 360°, 134.4^o + 103.0^o + 120.8^o = 358.2^o, and indicate that each the K_3I^{2+} cluster has a trigonal plane form. Each of these, three K^+ ions lie on an edge of the trigonal plane and the I^- ion is in the center of the plane.

Summary

ZnI_2 molecules are synthesized into the molecular-dimensioned cavities of $|K_6Zn_3(KI)_3(ZnI_2)_{0.5}|[Si_{12}Al_{12}O_{48}]$-**LTA** thorough the dynamic ion-exchange of $|Zn_6|[Si_{12}Al_{12}O_{48}]$-**LTA** and KI in CH_3OH solution at 294 K. The crystal structure of the product $(|K_6Zn_3(KI)_3(ZnI_2)_{0.5}|[Si_{12}Al_{12}O_{48}]$-**LTA**, a = 12.1690(10) Å) was determined at 294 K by single-crystal X-ray diffraction in the space group $Pm\overline{3}m$ with the final error index R_1 = 0.078 for 431 reflections which $F_o > 4\sigma(F_o)$. Half a Zn^{2+} ion and one I^- ion per unit cell are found in the sodalite cavities, indicating the formation of a ZnI_2 molecule per unit cell in 50% of the sodalite cavities. Additionally, three I^- ions per unit cell are also found opposite a 4-ring in the large cavity and form two K_2ZnI^{3+} and a K_3I^{2+} ionic clusters with K^+ and Zn^{2+} ions. The ZnI_2 molecules in the sodalite cavities are probably highly resistant to heating and dehydration because they are stabilized by interactions with the framework atoms. The ZnI_2 molecules are effectively synthesized in the sodalite cavities by dynamic ion-exchange method.

Supporting Information: Observed and calculated structure factors for $|K_6Zn_3(KI)_3(ZnI_2)_{0.5}|[Si_{12}Al_{12}O_{48}]$-**LTA**.

References

1. Naccache, C.; Taarit, Y. B. *Zeolite: Science and Technology*; Martinus Nijhoff Publishers: The Hague, The Netherlands, 1984; pp 373-396.
2. Kim, H. S.; Kim, J. J.; Kwon, H. N.; Chung, M. J.; Lee, B. G.; Jang, H. G. *J. Catal.* **2002**, *205*, 226.
3. Rhodes, C. N.; Brown, D. R. *J. Chem. Soc. Faraday Trans.* **1993**, *89*, 1387.
4. Fraile, J. M.; Garcia, J. I.; Massam, J.; Mayoral, J. A.; Pires, E. *J. Molecular Catal. A: Chemical* **1997**, *123*, 43.
5. Garcia, J. I.; Mayoral, J. A.; Pires, E.; Brown, D. R.; Massam, *Catal. Lett.* **1996**, *37*, 261.
6. Kodomari, M.; Nagaoka, T.; Furusawa, Y. *Tetrahedron Lett.* **2001**, *42*, 3105.
7. Guisnet, M.; Perot, G. *Zeolite: Science and Technology*; Martinus Nijhoff Publishers: The Hague, The Netherlands, 1984; pp 397-420.
8. Derouane, E. G. *Zeolite: Science and Technology*; Martinus Nijhoff Publishers: The Hague, The Netherlands, 1984; pp 347-371.
9. Yasuda, M.; Tsuji, S.; Shigeyoshi, Y.; Bada, A. *J. Am. Chem. Soc.* **2002**, *124*, 7440.
10. Tyagi, P.; Vedeshwar, A. G. *Physical Review B* **2001**, *64*, 245406.
11. Tyagi, P.; Vedeshwar, A. G. *Phys. Stat. Sol. (a)* **2002**, *191*, 633.
12. Heo, N. H.; Kim, H. S.; Lim, W. T.; Seff, K. *J. Phys. Chem. B* **2004**, *108*, 3168.
13. Lim, W. T.; Choi, S. Y.; Kim, B. J.; Kim, C. M.; Lee, I. S.; Kim, S. H.; Heo, N. H. *Bull. Korean Chem. Soc.* **2005**, *26*, 1090.
14. Kim, S. H.; Lim, W. T.; Kim, G. H.; Lee, H. S.; Heo, N. H. *Bull. Korean Chem. Soc.* **2006**, *27*, 679.
15. Charnell, J. F. *J. Crystal Growth* **1971**, *8*, 291.
16. McCusker, L. B.; Seff, K. *J. Phys. Chem.* **1981**, *85*, 405.
17. Sheldrick, G. M., *SHELXL97, Program for the Refinement of Crystal Structures*; University of Göttingen: Germany, 1997.
18. Cruz, W. V.; Leung, P. C. W.; Seff, K. *J. Am. Chem. Soc.* **1978**, *100*, 6997.
19. Mellum, M. D.; Seff, K. *J. Phys. Chem.* **1984**, *88*, 3560.
20. Raghavan, N. V.; Seff, K. *J. Phys. Chem.* **1976**, *80*, 2133.
21. Leung, P. C. W.; Kunz, K. B.; Seff, K. *J. Phys. Chem.* **1975**, *79*, 2157.
22. Doyle, P. A.; Turner, P. S. *Acta Crystallogr., Sect. A* **1968**, *24*, 390.
23. *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 71-98.
24. Cromer, D. T. *Acta Crystallogr.* **1965**, *18*, 17.
25. *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 148-150.
26. *Handbook of Chemistry and Physics, 64th ed.*; Chemical Rubber Co.: Cleveland, OH, 1983; p F-170.