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

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The positions of PbI_2 molecule synthesized into the molecular-dimensioned cavities of $|K_6(Pb_4I_2)(PbI_2)_{0.67}(H_2O)_2|[Si_{12}Al_{12}O_{48}]$-**LTA** have been determined. A single crystal of $|Pb_6|[Si_{12}Al_{12}O_{48}]$-**LTA**, prepared by the dynamic ion-exchange of $|Na_{12}|[Si_{12}Al_{12}O_{48}]$-**LTA** with aqueous 0.05 M $Pb(NO_3)_2$ and washed with deionized water, was placed in a stream of flowing aqueous 0.05 M KI at 294 K for three days. The resulting crystal structure of the product ($|K_6(Pb_4I_2)(PbI_2)_{0.67}(H_2O)_2|[Si_{12}Al_{12}O_{48}]$-**LTA**, $a = 12.353(1)$ Å) was determined at 294 K by single-crystal X-ray diffraction in the space group $Pm\overline{3}m$. It was refined with all measured reflections to the final error index $R_1 = 0.062$ for 623 reflections which $F_o > 4\sigma(F_o)$. 4.67 Pb^{2+} and six K^+ ions per unit cell are found at three crystallographically distinct positions: 3.67 Pb^{2+} and three K^+ ions on the 3-fold axes opposite six-rings in the large cavity, three K^+ ions off the plane of the eight-rings, and the remaining one Pb^{2+} ion lies opposite four-ring in the large cavity. 0.67 Pb^{2+} ions and 1.34 I^- ions per unit cell are found in the sodalite units, indicating the formation of a PbI_2 molecule in 67% of the sodalite units. Each PbI_2 (Pb-I = 3.392(7) Å) is held in place by the coordination of its one Pb^{2+} ion to the zeolite framework (a Pb^{2+} cation is 0.74 Å from a six-ring oxygens) and by the coordination of its two I^- ions to K^+ ions through six-rings (I-K = 3.63(4) Å). Two additional I^- ions per unit cell are found opposite a four-ring in the large cavity and form $Pb_2K_2I^{5+}$ and PbK_2I^{3+} moieties, respectively, and two water molecules per unit cell are also found on the 3-fold axes in the large cavity.

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

Introduction

Zeolites are crystalline microporous materials with tetrahedral framework structures enclosing cavities occupied by cations and (unless fully dehydrated) water molecules, both of which have enough freedom of movement to permit cation exchange and reversible dehydration.[1] These zeolites have about 30%-50% void space after dehydration, and have the potential to confine molecules or clusters up to a nanometer in diameter in a controlled fashion. This can lead to a wide range of applications including image plates for computerized x-ray radiography,[2,3] media for erasable optical memory,[2,3] electronic devices,[4,5] and gas storage.[6,7] Restricting the particle size to the nanometer scale has dramatic effects on the optical, electronic, vibrational, and thermodynamic properties of condensed matter.[8] Semiconductors are among the materials that can be confined within zeolites.[4,5]

Lead iodide (PbI_2) is a layered semiconductor material with a wide band gap energy ($E_g = 2.58$ eV), a high resistivity (10^{13} Ωcm), and a low-melting point (681 K). PbI_2 is an adequate charge carrier ($\mu\tau \sim 10^{-5}$ cm^2/V), and, because of its high density (6.2 g/cm^3) and high atomic number elements ($Z_{Pb} = 82$ and $Z_I = 53$), it has been used in room temperature solid state X-ray and γ-ray detectors.[9-12]

Shah *et al.* reported that they had made prototype detectors for X-ray imaging using PbI_2. Their experiments show high resolution and sensitivity for real time imaging, thus showing that the material had potential for medical applications.[13] Bhavsar *et al.*[14] noted that PbI_2 may find wide ranging application as a device material due to its photodecomposition, image recording capability, exciton spectra, electron spin resonance, Raman scattering effects, Franz-Keldysh effect, radiation damage, semiconducting properties, and polytype nature. Ponpon *et al.*[15] prepared the thin polycrystalline PbI_2 layers using a simple solution growth method on various substrates for the development of PbI_2 nuclear imaging devices. And they reported on their preliminary characterization in terms of electrical properties and optical response.

Many attempts to incorporate and characterize small PbI_2 clusters in zeolites have been made. Tang *et al.*[16] reported the absorption spectra for PbI_2, HgI_2, and BiI_3 clusters and molecules incorporated into large cavity of zeolite LTA at various loading densities. Their spectra exhibited bands originating from a molecule to five molecular clusters of PbI_2 and HgI_2, and from a monomer and a dimer of BiI_3. And they showed the excitation energies were largely shifted to the higher energy side compared with the respective bulk exciton energies, and shifted with decreasing the number of molecules, indicating the quantum size effect on the excitation energy. Togashi *et al.*[17] examined the PbI_2 clusters incorporated into the cages of LTA through a vapor phase after dehydration as a function of a cluster loading by X-ray diffraction and by electron microscopy. They suggested that

the clusters were formed inside the large cavity without destroying the framework and with a maximum loading density of *ca*. 3.8 PbI_2 clusters per large cavity.

In this work, fully Pb^{2+}-exchanged zeolite A ($|Pb_6|[Si_{12}Al_{12}O_{48}]$-**LTA**) was treated with aqueous KI in an attempt to synthesize nanoclusters of PbI_2 within the zeolite. 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**[18] and $|K_9(K_4Br)(Ag_4Br_4)_{0.75}|[Si_{12}Al_{12}O_{48}]$-**LTA**.[19]

Experimental Section

Large colorless single crystals of zeolite 4A (LTA), $|Na_{12}|[Si_{12}Al_{12}O_{48}]$-**LTA**, were synthesized by Kokotailo and Charnell.[20] 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. 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 $|Pb_6|[Si_{12}Al_{12}O_{48}]$-**LTA** were prepared by the dynamic (flow) ion-exchange of Na-A with aqueous 0.05 M $Pb(NO_3)_2$ (Aldrich 99.999%) at 294 K for 3 days.[21] The resulting Pb-A crystal was thoroughly washed with deionized water and then placed in a flowing stream of aqueous 0.05 M KI (Aldrich 99.99%) at 294 K for 3 days. 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. The crystal after ion-exchange with Pb^{2+} was colorless. After reaction

with KI, it became yellow.

X-ray diffraction data of the single-crystal was collected at 294(1) K on an ADSC Quantum210 detector at Beamline 4A MXW of PSL (Pohang Light Source, Pohang Accelerator Laboratory). The wavelength of the synchrotron X-rays was 0.69990 Å. The crystal was rotated through a total of 360°, with 1.0° oscillation per frame. We got basic scale file from program HKL2000 (Otwinowski & Minor, 1997) including the indexing program DENZO with the cubic space group *P23* and carried out the full-matrix least-squares refinement using SHELEX97[22] with the cubic space group *Pm$\bar{3}$m* (no systematic absences) in this work for reasons discussed previously.[21,23,24] A summary of the experimental and crystallographic data is presented in Table 1.

Structure Determination

Full-matrix least-squares refinement (SHELXL97)[22] was done on F_o^2 using all data. Refinement was initiated with the atomic parameters of the framework atoms [(Si,Al), O(1), O(2), and O(3)] (see Table 2) in dehydrated $|Pb_6|[Si_{12}Al_{12}O_{48}]$-**LTA**.[21] The initial refinement using isotropic thermal parameters for all positions converged to the error indices (defined in footnotes to Table 1) $R_1 = 0.52$ and $R_2 = 0.81$.

The progress of structure determination as subsequent peaks were found on difference Fourier functions and identified as non-framework atoms is given in Table 3. The refinement with eleven additional peaks from Fourier difference functions and isotropic thermal parameters to refine the framework atoms led to convergence with $R_1 = 0.078$ and $R_2 = 0.195$. These framework atoms and some atoms opposite 6-ring were allowed to refine anisotropically (see Table 2) and the refinement converged to $R_1 = 0.066$ and $R_2 = 0.160$. The final cycles of the refinement were carried out with occupancies fixed at the values given in Table 2 and 3. This model converged to the final error indices $R_1 = 0.062$ and $R_2 = 0.148$. 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 $a = 0.074$ and $b = 18.42$ as refined parameters (see Table 1). Atomic scattering factors for Pb^{2+}, I^-, K^+, O^-, and $(Si,Al)^{1.75+}$ were used.[25,26] 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 modified to account for anomalous dispersion.[27,28]

Results and Discussion

Zeolite A Framework and Cations. In the crystal structure of the crystal, $|K_6(Pb_4I_2)(PbI_2)_{0.67}(H_2O)_2|[Si_{12}Al_{12}O_{48}]$-**LTA**, the flex of (distortions to) the framework structure of this structure is much more like that of dehydrated $|K_{12}|[Si_{12}Al_{12}O_{48}]$-**LTA** and hydrated $|K_{12}|[Si_{12}Al_{12}O_{48}]$-**LTA**

Table 1. Summary of Experimental and Crystallographic Data

Crystal cross-section (mm)	0.08
Ion exchange for Pb^{2+} (days, mL)	3, 8
Washing with deionized water (K, days)	294, 1
Reaction of Pb-A with KI (days, mL)	3, 12
Temperature for data collection (K)	294(1)
X-ray source	PLS(4A MXW BL)[a]
Wavelength (Å)	0.69990
Space group, No.	*Pm$\bar{3}$m*, 221
Unit cell constant, *a* (Å)	12.353(1)
Maximum 2θ for data collection (deg)	61.93
No. of unique reflections measured, *m*	652
No. of reflections ($F_o > 4\sigma(F_o)$)	623
No. of variables, *s*	54
Data/parameter ratio, *m/s*	12.1
Weighting parameters : a/b	0.0741 / 18.4152
Final error indices	
R_1^b	0.062
R_2^c	0.148
Goodness-of-fit[d]	1.069

[a]Beamline 4A MXW of Pohang Light Source. $^bR_1 = \Sigma|F_o - |F_c||/\Sigma F_o$; R_1 is calculated using only the 623 reflections for which $F_o > 4\sigma(F_o)$. $^cR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; R_2 is calculated using all 652 unique reflections measured. ^{d}Goodness-of-fit = $(\Sigma w(F_o^2 - F_c^2)^2/(m-s))^{1/2}$.

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	1849(1)	3744(1)	0(7)	0(7)	0(7)	0	0	13(5)	24[c]	
O(1)	12(h)	0	2357(5)	5000[d]	299(32)	177(27)	126(25)	0	0	0	12	
O(2)	12(i)	0	2855(4)	2855(4)	535(45)	107(16)	107(16)	0	0	61(20)	12	
O(3)	24(m)	1114(3)	1114(3)	3524(4)	286(15)	286(15)	254(21)	155(19)	40(15)	40(15)	24	
Pb(1)	8(g)	2221(1)	2221(1)	2221(1)	155(4)	155(4)	155(4)	24(2)	24(2)	24(2)	3	3.1(1)
Pb(1')	8(g)	1572(2)	1572(2)	1572(2)	179(8)	179(8)	179(8)	53(10)	53(10)	53(10)	0.67	0.68(2)
K(1)	8(g)	2784(17)	2784(17)	2784(17)	477(74)	477(74)	477(74)	35(73)	35(73)	35(73)	1	1.0(7)
K(1')	8(g)	2912(61)	2912(61)	2912(61)	3398(662)						2	1.3(8)
Pb(2)	48(n)	1860(59)	3927(55)	4659(91)	3111(461)						1	1.3(4)
K(2)	24(m)	537(38)	4548(25)	4548(25)	1079(147)						2	1.6(3)
K(2')	24(m)	1123(29)	4377(21)	4377(21)	273(63)						1	2.2(4)
I(1)	8(g)	1087(7)	1087(7)	1087(7)	1011(35)						1.34	1.21(6)
I(2)	12(j)	2657(32)	2657(32)	5000[d]	1915(178)						1	0.8(3)
I(3)	48(n)	2434(80)	3371(88)	4384(90)	2146(437)						1	1.3(7)
O(4)	8(g)	4411(84)	4411(84)	4411(84)	3938(1918)						2	5.3(13)

[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[e]	
	Pb(1)	Pb(1')	K(1)	K(1')	Pb(2)	K(2)	K(2')	I(1)	I(2)	I(3)	O(4)	R_1	R_2
1[a]												0.52	0.81
2	3.3(1)											0.20	0.49
3	2.9(4)		1.8(17)									0.20	0.48
4	3.0(3)	0.8(1)	2.1(14)									0.14	0.35
5	2.8(2)	0.7(1)	2.7(12)					1.4(1)				0.11	0.27
6	2.8(2)	0.7(1)	2.6(12)		3.3(4)			1.2(1)				0.107	0.256
7	2.8(2)	0.7(1)	2.6(11)			1.2(3)	2.6(4)	1.3(1)				0.104	0.249
8	2.8(2)	0.7(1)	2.3(10)	1.7(3)		1.1(3)	2.6(4)	1.3(1)				0.100	0.235
9	2.8(2)	0.7(1)	1.9(8)	1.4(2)		1.3(3)	3.2(4)	1.2(1)				0.089	0.217
10	2.8(2)	0.7(1)	1.8(8)	1.7(3)	3.1(5)	1.2(3)	1.9(4)	1.3(1)	1.0(3)			0.082	0.204
11	2.8(2)	0.7(1)	1.9(8)	1.8(3)	1.2(3)	1.3(3)	2.7(4)	1.3(1)	1.0(2)		12.5(50)	0.078	0.196
12	2.7(2)	0.7(1)	1.9(8)	1.6(3)	1.3(4)	1.4(3)	2.5(5)	1.2(1)	1.3(3)	1.3(9)	3.9(17)	0.078	0.195
13[b]	2.7(1)	0.7(1)	2.0(7)	1.5(2)	1.4(1)	1.5(3)	2.3(4)	1.2(1)	1.3(2)	1.2(8)	4.1(15)	0.066	0.165
14[c]	3.1(1)	0.68(2)	1.0(7)	1.3(8)	1.3(4)	1.6(3)	2.2(4)	1.21(6)	0.8(3)	1.3(7)	5.3(13)	0.066	0.160
15[c,d]	3	0.67	1	2	1	2	1	1.34	1	1	2	0.0618	0.1482

[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. [e]Defined in footnotes to Table 1.

than that of $|Pb_6|[Si_{12}Al_{12}O_{48}]$-**LTA** (see Table 5).[21.29]

In the crystal structure of the zeolite $|K_6(Pb_4I_2)(PbI_2)_{0.67}$-$(H_2O)_2|[Si_{12}Al_{12}O_{48}]$-**LTA**, 4.67 Pb^{2+} and six K^+ ions per unit cell are distributed over three crystallographically distinct positions: on the 3-fold axes opposite six-ring, three and 0.67 Pb^{2+} ions are found at Pb(1) and Pb(1'), respectively, and one and two K^+ ions at K(1) and K(1') are also found, respectively. And, two and one K^+ ions at K(2) and K(2') are found on eight-rings, respectively, and a Pb^{2+} ion at Pb(2) is found on opposite four-ring in the large cavities. Therefore, the eight six-rings per unit cell contains 6.67 Pb^{2+} and three

K^+ ions; each Pb^{2+} and K^+ ion lies on a 3-fold axis and those ions at Pb(1), Pb(1'), K(1), and K(1') extend 0.65, 0.74, 1.85, and 2.13 Å, respectively, into the large cavity from the (111) planes at O(3) (see Table 6).

The Pb^{2+} ions at Pb(1) and Pb(1') are in the large cavities and in the sodalite units, respectively. Considering the sum of ionic radii of Pb^{2+} and O^{2-}, r_{Pb}^{2+} (1.20 Å) $+ r_O^{2-}$ (1.32 Å) $= 2.52$ Å,[30] The approach distance from the Pb^{2+} ions on the 3-fold axis to O(3), Pb(1)-O(3) = 2.516(5) Å and Pb(1')-O(3) = 2.541(5) Å, are very similar to the calculated bonding distance, and are close to the distances of Pb^{2+} to framework

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

Distances			Angles	
(Si,Al)-O(1)	1.674(3)	O(1)-(Si,Al)-O(2)	109.4(3)	
(Si,Al)-O(2)	1.6586(16)	O(1)-(Si,Al)-O(3)	110.77(20)	
(Si,Al)-O(3)	1.6707(16)	O(2)-(Si,Al)-O(3)	107.44(21)	
		O(3)-(Si,Al)-O(3)	110.9(4)	
Pb(1)-O(3)	2.516(5)			
Pb(1')-O(3)	2.541(5)	(Si,Al)-O(1)-(Si,Al)	136.0(4)	
K(1)-O(3)	3.058(23)	(Si,Al)-O(2)-(Si,Al)	172.9(4)	
K(1')-O(3)	3.23(9)	(Si,Al)-O(3)-(Si,Al)	150.3(3)	
K(2)-O(1)	2.84(3)			
K(2)-O(2)	3.03(5)	O(3)-Pb(1)-O(3)	113.6(1)	
K(2')-O(1)	2.957(23)	O(3)-Pb(1')-O(3)	111.91(15)	
K(2')-O(2)	3.00(4)	O(3)-K(1)-O(3)	87.0(8)	
Pb(2)-O(1)	3.04(7)	O(3)-K(1')-O(3)	81(3)	
Pb(2)-O(2)	3.46(9)			
		I(1)-Pb(1')-I(1)	68.1(4)	
Pb(1')-I(1)	3.392(7)	O(3)-Pb(1')-I(1)	84.98(17),	
			147.2(3)	
K(1)-I(1)	3.63(4)	Pb(1)-I(2)-Pb(1)	155.0(18)	
Pb(1)-I(2)	3.517(12)	Pb(1)-I(2)-K(2)	80.5(7), 98.1(5)	
K(2)-I(2)	3.55(4)	K(2)-I(2)-K(2)	173.6(22)	
K(1)-I(3)	3.60(11)	K(1)-I(3)-K(2')	78.1(22)	
K(2')-I(3)	3.56(11)	K(1)-I(3)-Pb(2)	87.3(3)	
Pb(2)-I(3)	3.37(15)	K(2')-I(3)-Pb(2)	151.0(3)	
K(1')-O(4)	3.21(22)	K(1')-O(4)-O(4)	180(10)	
		O(3)-K(1')-O(4)	131.2(18)	
O(4)-O(4)	2.5(4)			
I(1)···I(1)	3.799(23)			
I(1)···O(3)	3.010(10)			
I(2)···O(3)	3.25(5)			
I(3)···O(1)	3.4(10)			

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

oxygen that were found in previous works (2.46 Å to 2.71 Å).[21]

K(1) and K(1') are 3.058(23) Å and 3.23(9) Å away from its three O(3) oxygens, respectively (see Table 4) and these distances are much longer than the sum of the ionic radii of K^+ and O^{2-}, 1.33 Å + 1.32 Å = 2.65 Å.[30] Such somewhat longer approach distances from framework oxygens can be explained by all of K^+ ions at K(1) and K(1') making clusters with I^- anions 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**.[29] The K^+ ions at K(1) and K(1') extend 1.85 Å and 2.13 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) = 87.0(8)° and O(3)-K(1')-O(3) = 81.3(3)°.

Two and one K^+ ions at K(2) and K(2'), respectively, occupy the three eight-rings per unit cell. The K^+ ions at K(2) and K(2') are 2.84(3) Å and 2.957(23) Å from framework oxygen at O(1), respectively. The approach distance is somewhat longer than the calculated one, 2.65 Å, but the longer distances of eight-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 eight-ring cations can be explained by existence of two kinds of K^+-included clusters near eight-rings in the large cavities (*vide infra*).

One Pb^{2+} ion per unit cell at Pb(2) is located opposite four-ring in the large cavity and is 3.04(7) Å from framework oxygen O(1). The Pb(2)-O(1) approach distance, 3.04(7) Å, is somewhat longer than the sum of ionic radii of Pb^{2+} and O^{2-}, 2.52 Å, but the distance can be considerable because each of these Pb^{2+} ions at Pb(2) are bonded to a I^- ion and make Pb-K-I clusters (*vide infra*). Therefore, the Pb^{2+} ions at Pb(2) are bonded to I^- ions and get away from framework oxygens, O(1) and O(2).

Including all of the cationic ions that are found, the total charge of the unit cell is +3.34 ((4.67 × (+2)) + (6.0 × (+1)) − 12 = +3.34), because occupancies of all of Pb^{2+} and K^+ ions per unit cell are 4.67 and 6.0, 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 and are found as Table 2 and 3.

PbI$_2$ Molecule in the Sodalite Unit. 0.67 Pb^{2+} ions and 1.34 I^- ions per unit cell occupy nonequivalent 3-fold axes positions in the sodalite units, indicating a PbI_2 molecule is formed in 67% of the sodalite units. The 0.67 Pb^{2+} ions at Pb(1') lies opposite a six-ring in the sodalite unit and the 1.34 I^- ions at I(1) occupy similar positions, recessed more deeply into the sodalite unit. It is impossible for both a Pb^{2+} and a I^- ion to approach the same six-ring because their approach distance, 1.037(14) Å, would be too short.

The Pb^{2+} ion at Pb(1') is 2.516(5) Å from three six-ring oxygens at O(3) (see Table 3) and extend 0.74 Å into the sodalite unit from the (111) planes at O(3) (see Table 4). Considering the ionic radii of the framework oxygens to be

Table 5. (Si,Al)-O-(Si,Al) Angles (deg)[a] at Framework Oxygens and Unit Cell Parameters for K^+- and Pb^{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)
$|Pb_6|[Si_{12}Al_{12}O_{48}]$-**LTA**[c]	164(2)	148(1)	138(1)	12.162(2)
$|Pb_9(OH)_8(H_2O)_3|[Si_{12}Al_{12}O_{48}]$-**LTA**[c]	156(2)	155(2)	137(1)	12.225(3)
$|K_6(Pb_4I_2)(PbI_2)_{0.67}(H_2O)_2|[Si_{12}Al_{12}O_{48}]$-**LTA**[d]	136.0(4)	172.9(4)	150.3(3)	12.353(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 29. [c]Reference 21. [d]This work.

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

	|K₆(Pb₄I₂)(PbI₂)₀.₆₇(H₂O)₂|-**LTA**[b]	|Pb₆|-**LTA**[c]	|Pb₉(OH)₈(H₂O)₃|-**LTA**[c]	Dehydrated |K₁₂|-**LTA**[d]	Hydrated |K₁₂|-**LTA**[d]
Pb(1)	0.65	1.22	1.19		
Pb(1')	−0.74				
Pb(2)		−1.50	−1.61		
Pb(4)			0.29		
K(1)	1.85			0.79	1.49
K(1')	2.13				
K(3)				3.45	5.26
K(4)				−1.35	
K(5)				−0.19	
I(1)	−1.78				
O(4)	5.34				3.34
O(5)			−1.94		

[a]A positive deviation indicate 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 21. [d]Reference 29.

1.32 Å,[30] the ionic radii of this Pb^{2+} ion must be 2.516−1.32 = 1.196 Å. This is very similar to the tabulated ionic radius of Pb^{2+}, 1.20 Å,[34] indicating that it is a Pb^{2+} ion that is at Pb(1).

The 1.34 I^- ions at I(1), the occupancy of these ions are equal to twice of that of Pb^{2+} ion at Pb(1'), extend 1.78 Å into the sodalite unit from the (111) planes at O(3) (see Table 4). They are thus far from the three nearest anionic framework oxygens, indicating that they are not cations. Furthermore, the bonding distance to the closely approach Pb^{2+} ion at Pb(1') is 3.392(7) Å, similar to the sum of ionic radii of Pb^{2+} and I^-, r_{Pb}^{2+} (1.20 Å) + r_I^- (2.16 Å) = 3.36 Å.[30] The I^- ions lie on the other side of six-rings that are occupied with K^+ ions at K(1) or K(1') in the large cavities or with nothing because the approach distances between I(1) and the other positions, Pb(1) and Pb(1'), are too short to co-exist in a same six-ring (Pb(1)-I(1) = 2.425(14) Å and Pb(1')-I(1) = 1.037(14) Å). But, the I^- ions at I(1) can bond to up to K^+ ions at K(1) opposite adjacent six-rings (K(1)-I(1) = 3.63(4) Å). Considering the sum of ionic radii between K^+ and I^-,

r_K^+ (1.33 Å) + r_I^- (2.16 Å) = 3.49 Å,[30] and esd, the distances between K(1) and I(1) are reasonable.

Considering the occupancies of 0.67 Pb^{2+} ions at Pb(1) and 1.34 I^- ions at I(1) per unit cell and the possible arrangements of Pb^{2+} and I^- ions within the space of the sodalite unit, one PbI_2 molecule in the 67% of the sodalite units is most likely (see Figure 1 and 2). In this arrangement, one Pb^{2+} ion bonds to two I^- ions (in addition to three framework oxygens), and each I^- ion bonds to one Pb^{2+} ion (in addition to one or none K^+ ion at K(1)). The stereoview of such a sodalite unit with a PbI_2 molecule is shown in Figure 1.

The PbI_2 molecules in the sodalite unit are probably more stable than those in the large cavities synthesized by previous works[17] because absorbed and captured molecules in the smaller cages have more resistance to high temperature and sudden changes of temperature and vacuum. Additionally, the synthetic method, dynamic ion-exchange with aqueous solutions in room temperature, is more productive and efficient compared to that of previous works[17] including
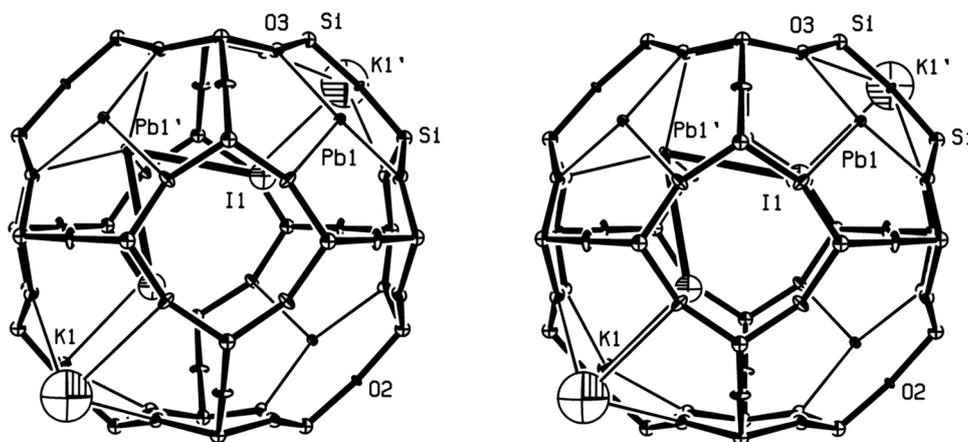
Figure 1. A stereoview of a sodalite unit in \|K₆(Pb₄I₂)(PbI₂)₀.₆₇(H₂O)₂\|[Si₁₂Al₁₂O₄₈]-**LTA**. 67% of the sodalite cavities contain a PbI_2 molecule (heavy lines) as shown. One Pb^{2+} at Pb(1') coordinate to three O(3) oxygens. The zeolite A framework is drawn with bonds of medium thickness between oxygens and tetrahedrally coordinated (Si,Al) atoms. The coordinations of K^+ and Pb^{2+} ions to oxygens of zeolite framework are indicated by the thinnest lines. Ellipsoids of 20% probability are shown.
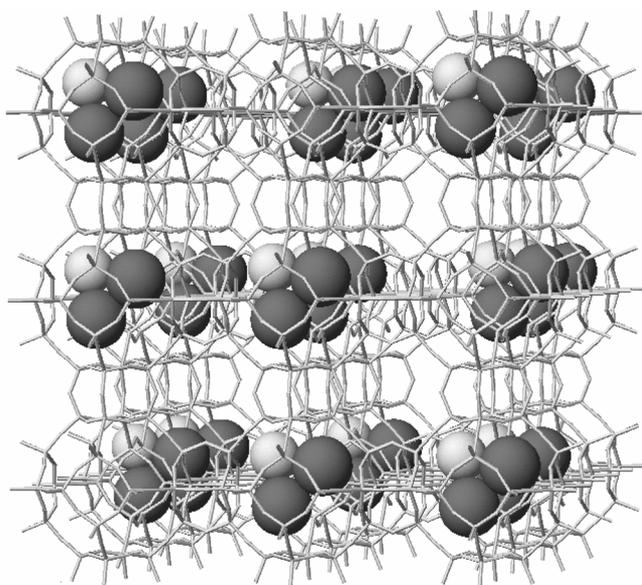
Figure 2. The PbI_2 molecules in alternating sodalite cavities of several unit cells. For clarity, the framework atoms have been simplified and the cations have been omitted. The long-range ordering and identical orientations of the nanoparticles shown here is reasonable, but it has not been established in this work.

dehydration and reaction with PbI_2 vapor.

Pb-K-I Moieties in the Large Cavity. Two I^- ions per unit cell are found opposite four-rings in the large cavity: one and one at $I(2)$ and $I(3)$ per unit cell are opposite four-ring in the large cavities, respectively, but the I^- ions at $I(2)$ and those at $I(3)$ are found at two different positions (see Table 2). Therefore, two kinds of moieties including an I^- ion at $I(2)$ or $I(3)$ are predicted: one moiety including an I^- ion at $I(2)$, the other including an I^- ion at $I(3)$.

$Pb_2K_2I^{5+}$ cluster is consisted with two K^+ ions at $K(2)$, two Pb^{2+} ions at $Pb(1)$, and an I^- ion at $I(2)$ in the large cavity and has a tetragonal plane form with center at $I(2)$ (see Figure 3 and 4(a)). The approach distances of $Pb(1)-I(2)$ and $K(2)-I(2)$ are 3.517(12) Å and 3.55(4) Å, respectively. The distances are reasonable with esds as compare with the

calculated distance of 3.36 Å and 3.49 Å for Pb-I and K-I, respectively. The angles are also reasonable with a good geometry of the moiety, too $(Pb(1)-I(2)-Pb(1) = 155.0(18)^\circ$, $K(2)-I(2)-K(2) = 173.6(22)^\circ$, and $Pb(1)-I(2)-K(2) = 80.5(7)^\circ$ and $98.1(5)^\circ$). Additionally, the somewhat long distance of $K(2)-O(1)$, 2.84(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 $Pb_2K_2I^{5+}$ moiety.

The other Iodide ion per unit cell is found at $I(3)$, opposite a four-ring in the large cavity. It bonds to two K^+ ions (one at $K(1)$ and one at $K(2')$) and Pb^{2+} ion at $Pb(2)$, in a trigonal plane manner to give a PbK_2I^{3+} cluster (see Figure 3 and 4(b)). The bonding distances of $Pb(2)-I(3)$, $K(1)-I(3)$, and $K(2')-I(3)$ are 3.37(15) Å, 3.60(11) Å, and 3.56(11) Å, respectively. These are very close to the sum of ionic radii, 3.36 Å and 3.49 Å for Pb-I and K-I,[30] respectively, considering esds. Because these Pb^{2+} and K^+ ions bond to I^- ions at $I(3)$ with their reasonable distances and structure, these cations lie on far away from framework oxygens at $O(3)$ (*vide supra*). The angles of $K(1)-I(3)-K(2')$, $K(1)-I(3)-Pb(2)$, and $K(2')-I(3)-Pb(2)$ are $78.1(22)^\circ$, $87.3(3)^\circ$, and $151.0(3)^\circ$, respectively. Each of these cations, K^+ and Pb^{2+}, lie on an edge of trigonal plane and the I^- ion is the center of the plane.

Water Molecules in the Large Cavity. Two non-framework oxygens at $O(4)$ per unit cell are found on the 3-fold axes opposite six-ring in the large cavity. The position of O^{2-} ions at $O(4)$, extend 5.34 Å into the large cavity from the (111) planes at $O(3)$ and cann't make any bond to framework oxygens. Therefore, the O^{2-} ions at $O(4)$, maybe consisting water molecules, must be bonded to the other cations and the nearest cations are K^+ ions at $K(1')$ $(K(1')-O(4) = 3.21(22)$ Å). The distance is much longer than the sum of ionic radii of K^+ and O^{2-}, but the distance is possible considering the geometry of the moiety consisted with two K^+ ions at $K(1')$ and two O^{2-} ions at $O(4)$ (see Figure 3 and 4(c)). The linear moiety, $K^+-O \cdots O-K^+$, is expected with ionic bonds of K^+-O^{2-} and hydrogen bonds between water molecules. The bonding distances of $K(1')-O(3)$ and $K(1')-O(4)$ are 3.23(9) Å and 3.21(22) Å, respectively and these two similar
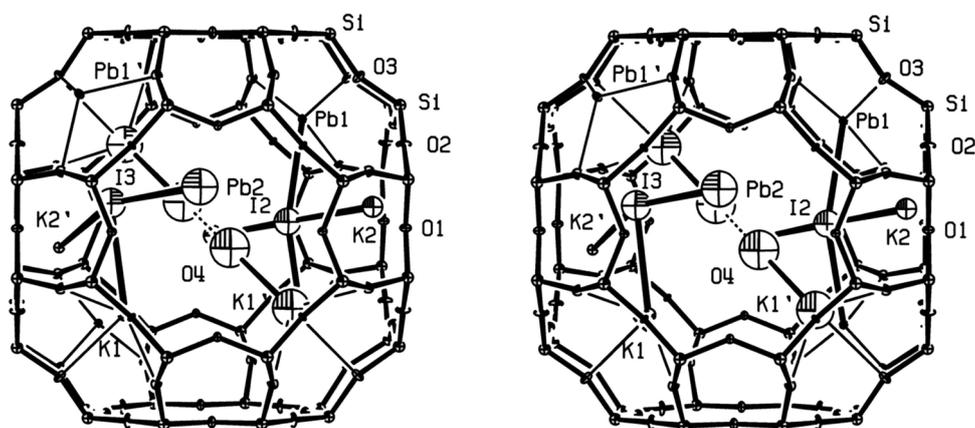
Figure 3. Stereoview of the large cavity of $|K_6(Pb_4I_2)(PbI_2)_{0.67}(H_2O)_2|[Si_{12}Al_{12}O_{48}]$-**LTA** with a $Pb_2K_2I^{5+}$ and a PbK_2I^{3+} moieties and two water molecules. Heavy lines indicate K^+-I^- and $Pb^{2+}-I^-$ bonds. See the caption to Figure 1 for other details.
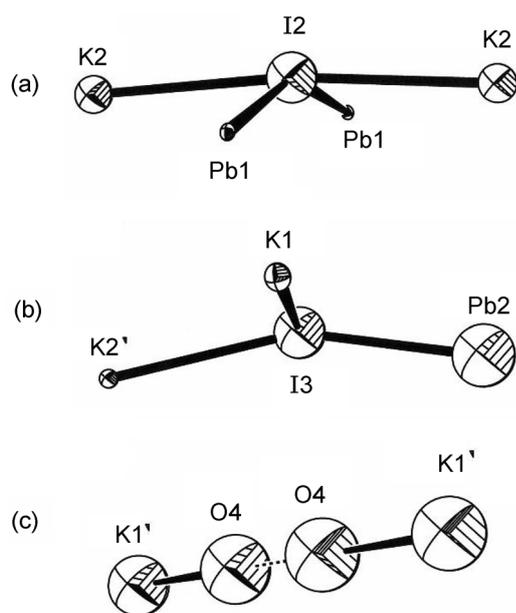
Figure 4. Views of three kinds of moieties found in the large cavity of $|K_6(Pb_4I_2)(PbI_2)_{0.67}(H_2O)_2|[Si_{12}Al_{12}O_{48}]$-**LTA**: (a) $Pb_2K_2I^{5+}$, (b) PbK_2I^{3+}, and (c) $K(1')$-$O(4)\cdots O(4)$-$K(1')$.

distances of $K(1')$-$O(3)$ and $K(1')$-$O(4)$ are also expected by the well-balanced $O(3)$-$K(1')$-$O(4)$ structure (the K^+ ion at $K(1')$ is at the balance point of the structure). The distance of $O(4)$-$O(4)$ is 2.5(4) Å, similar to the hydrogen bonding distance with esds and the angle of $K(1')$-$O(4)\cdots O(4)$ is $180(10)^\circ$. Therefore, two water molecules per unit cell are lie on near deep inside of the large cavity with hydrogen bonds to each other and each of these molecules is bonded to a K^+ ion at $K(1')$.

According to the varied occupancy of $O(4)$, 5.3(13) per unit cell (see Table 2), not only two oxygens at $O(4)$ per unit cell but three or four oxygens are also possible at the positions. The final error indices, R_1, are 0.0618, 0.0615, and 0.0618 for final structures including two, three, and four oxygens at $O(4)$, respectively. The crystal structure with three oxygens at $O(4)$ is a little better than those with two and four by the final error indices. But there aren't enough space to exist more than two oxygens at $O(4)$ in the large cavity considering to the other moieties such as $Pb_2K_2I^{5+}$ and PbK_2I^{3+} clusters: The nearest distances of $O(4)$-$I(2)$ and $O(4)$-$I(3)$ are too short, 2.9 Å to 3.0 Å, compared to ionic radii of O^{2-} and I^- when three or four oxygens are at $O(4)$ in a large cavity. Therefore, the crystal structure including only two oxygens at $O(4)$ per unit cell is most expected with the symmetric K^+-$O\cdots O$-K^+ geometry, the balanced $K(1')$ position, and the reasonable distance to the other anions.

Summary

PbI_2 molecules are synthesized into the molecular-dimensioned cavities of $|K_6(Pb_4I_2)(PbI_2)_{0.67}(H_2O)_2|[Si_{12}Al_{12}O_{48}]$-**LTA** by the dynamic ion-exchange of $|Pb_6|[Si_{12}Al_{12}O_{48}]$-**LTA** and aqueous KI at 294 K. The crystal structure of the product ($|K_6(Pb_4I_2)(PbI_2)_{0.67}(H_2O)_2|[Si_{12}Al_{12}O_{48}]$-**LTA**, a = 12.353(1) Å) was determined at 294 $\underline{K}$ by single-crystal X-ray diffraction in the space group $Pm\bar{3}m$ with the final error index R_1 = 0.062 for 623 reflections which $F_o > 4\sigma(F_o)$. 0.67 Pb^{2+} ions and 1.34 I^- ions per unit cell are found in the sodalite units, indicating the formation of a PbI_2 molecule per unit cell in 67% of the sodalite units. Additionally, two I^- ions per unit cell are also found opposite a four-ring in the large cavity and form a $Pb_2K_2I^{5+}$ and a PbK_2I^{3+} moieties with K^+ and Pb^{2+} ions and two water molecules per unit cell are also found on the 3-fold axes in the large cavity.

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