

Crystal Structure of Zeolite X Exchanged with Pb(II) at pH 6.0 and Dehydrated: $(\text{Pb}^{4+})_{14}(\text{Pb}^{2+})_{18}(\text{Pb}_4\text{O}_4)_8\text{Si}_{100}\text{Al}_{92}\text{O}_{384}$

Young Hoon Yeom and Yang Kim*

Department of Chemistry, Pusan National University, Pusan 609-735, Korea

Karl Seff*

Department of Chemistry, University of Hawaii, 2545 The Mall, Honolulu, Hawaii 96822

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A single crystal of zeolite X was 39% overexchanged with aqueous Pb^{2+} at pH 6.0. After dehydration at 420 °C and 2×10^{-6} Torr, its crystal structure was determined by X-ray diffraction techniques in the cubic space group $Fd\bar{3}$ at 21 °C ($a = 25.238(5)$ Å). The structure, $\text{Pb}_{64}\text{O}_{32}-\text{Si}_{100}\text{Al}_{92}\text{O}_{384}$ per unit cell, was refined to the final error indices $R_1 = 0.080$ and $R_2 = 0.070$ with 486 reflections for which $I > 3\sigma(I)$. Pb^{4+} formed upon evacuation at elevated temperature by a reaction which can be written, per unit cell, as $64 \text{Pb}^{2+} + 36 \text{OH}^- \rightarrow 18 \text{Pb}^{2+} + 8 \text{Pb}_4\text{O}_4 + 14 \text{Pb}^{4+} + 14 \text{H}_2 + 4 \text{H}_2\text{O}$. Pb ions occupy three nonequivalent sites. Each of 14 lead ions at site II is nearly in a six-ring plane where it coordinates to three framework oxygens at 2.32(2) Å and to a nonframework oxygen at 2.24(2) Å; these short distances indicate that these are Pb^{4+} . Eighteen Pb^{2+} ions, also at site II, are 2.54(2) Å from three framework oxygens and 2.95(2) Å from a nonframework oxygen. Each sodalite cage is filled by a nearly cubic Pb_4O_4 cluster with Pb^{2+} and O^{2-} ions alternating; the four Pb^{2+} ions (32 per unit cell) are at site I'; each is 2.67(2) Å from three framework oxygens and 2.59(3) Å from three nonframework oxygens. Each Pb_4O_4 cube bonds radially *via* its oxygens through six-rings to four additional lead ions (Pb^{2+} and Pb^{4+}) to give larger cationic clusters, perhaps predominantly of formula $[\text{Pb}_8\text{O}_4]^{12+}$. The 18 Pb^{2+} ions which are external to the Pb_4O_4 cubes appear to have axial nonbonding lone pairs which extend into the supercage.

Introduction

Hertzenberg and Sherry observed a small overexchange of Pb^{2+} into zeolite Na-A from 0.1 M $\text{Pb}(\text{NO}_3)_2$.¹ This effect was not seen when Ca-A was used.² Wiers *et al.*² suggested that H^+ -exchange may be responsible for the differing pH's of aqueous slurries (that is, of the solution after equilibrium between a zeolite sample and water) of Na-A and Ca-A. Together, these observations suggest that the extent of exchange could depend on pH if flow methods are used.

The crystal structure of $\text{Pb}_9\text{O}(\text{OH})_4\text{-A}$, Na-A exchanged with Pb^{2+} at pH 6.0 and evacuated at 26 °C, showed that a 50% overexchange of Pb^{2+} had occurred.³ The structure of Na-A ion-exchanged with ultrapure Pb^{2+} acetate at pH 6.0 and dehydrated under vacuum at 450 °C, $\text{Pb}_9(\text{OH})_8(\text{H}_2\text{O})_3\text{-A}$, verified that a 50% overexchange of Pb^{2+} had occurred due to cation hydrolysis.⁴ Also, it appeared that one of the Pb^{2+} ions had been oxidized to Pb^{4+} because of the very short approaches it made to framework oxygens. On the other hand, if ion exchange was done by flow methods with 0.1 M $\text{Pb}(\text{NO}_3)_2$ (pH 4.3), only fractionally more than six Pb^{2+} ions (the stoichiometric number), 6.3, exchange into the zeolite.^{1,4}

More recently, $[\text{Pb}_4(\text{OH})_4]^{4+}$ clusters have been reported in the sodalite cages of Pb^{2+} -overexchanged zeolite X.⁵ These $[\text{Pb}_4(\text{OH})_4]^{4+}$ clusters fully occupy the sodalite cages in the hydrated zeolite, but upon partial dehydration about one-third of these Pb^{2+} ions migrate from the sodalite cages into the large cavities.⁵

Lead has a well-defined cationic chemistry in aqueous solution.^{6–8} Pb^{2+} is partially hydrolyzed in water.^{7,9} The compositions of equilibrium mixtures from the hydrolysis of

Pb^{2+} has been investigated by a variety of techniques such as potentiometric titration,⁹ vibrational analysis,¹⁰ Pb-207 NMR,¹¹ Raman spectroscopy,¹² and theoretical calculation.¹³ The complexation between Pb^{2+} and hydroxide has been studied in molten (K,Na)NO₃ at 280 °C by various techniques.¹⁴ The following species have been reported in the lead hydroxide system: $\text{Pb}(\text{OH})_3^-$, $\text{Pb}(\text{OH})_2$, PbOH^+ , $\text{Pb}_2(\text{OH})_2^{2+}$, $\text{Pb}_2\text{OH}^{3+}$, $\text{Pb}_3(\text{OH})_5^+$, $\text{Pb}_3(\text{OH})_4^{2+}$, $\text{Pb}_3(\text{OH})_3^{3+}$, $\text{Pb}_4(\text{OH})_4^{4+}$, $\text{Pb}_4(\text{OH})_2^{6+}$, and $\text{Pb}_6(\text{OH})_8^{4+}$.^{9,13,15,16} The following lead oxide hydroxide clusters have been characterized by single-crystal X-ray diffraction methods: $[\text{Pb}_6\text{O}(\text{OH})_6]^{4+}$ in α - and β - $\text{Pb}_6\text{O}(\text{OH})_6(\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$,^{17,18} $\text{Pb}_4(\text{OH})_4^{4+}$ in $\text{Pb}_4(\text{OH})_4(\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$ ¹⁹ and in $(\text{Pb}_4(\text{OH})_4)_3\text{CO}_3(\text{ClO}_4)_{10} \cdot 6\text{H}_2\text{O}$,²⁰ and $[\text{Pb}_4(\text{OPb})_4]^{8+}$ in $\text{TlPb}_8\text{O}_4\text{Br}_9$ ²¹ and $\text{Pb}_9\text{O}_4\text{Br}_{10}$.²²

This work was done to investigate the behavior of Pb^{2+} in zeolite X, with the hope of preparing lead oxide clusters, such as Pb_4O_4 or $[\text{Pb}_8\text{O}_4]^{8+}$. In addition, we wished to see whether Pb^{4+} would form upon dehydration at high temperature, as it appeared to have in zeolite A.⁴

Experimental Section

Large single crystals of sodium zeolite X, stoichiometry $\text{Na}_{92}\text{Si}_{100}\text{Al}_{92}\text{O}_{384}$ per unit cell, were prepared in St. Petersburg, Russia.²³ One of these, a colorless octahedron about 0.25 mm in cross section, was lodged in a fine Pyrex capillary. Ion exchange was accomplished by flow methods: 0.05 M $\text{Pb}(\text{O}_2\text{CCH}_3)_2$ solution, pH 6.0, was allowed to flow past the crystal at a velocity of approximately 1.5 cm/s for 72 h at 17 °C. The crystal was washed by continuing this procedure using distilled water for *ca.* 10 h at 17 °C after ion exchange. The crystal in a finely drawn Pyrex capillary was attached to a vacuum system and cautiously dehydrated by gradually increasing its temper-

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TABLE 1: Positional, Thermal,^a and Occupancy Parameters for Dehydrated Pb₆₄O₃₂-X

atom	wyc. pos.	site	x	y	z	U ₁₁ ^b or U _{iso} ^d	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃	occupancy ^c		
												varied	fixed	
Si	96(g)		-546(4)	1257(4)	353(3)	114(13)								96
Al	96(g)		-569(4)	367(3)	1249(4)	127(25)								96
O(1)	96(g)		-1074(9)	1(8)	1047(9)	317(63)								96
O(2)	96(g)		3(8)	-32(8)	1408(8)	279(63)								96
O(3)	96(g)		-350(8)	796(8)	764(8)	266(51)								96
O(4)	96(g)		-664(8)	678(8)	1834(8)	253(63)								96
Pb(1)	32(e)	I'	7051(7) ^a	7051(7)	7051(7)	629(8)	629(8)	629(8)	-225(9)	-225(9)	-225(9)	33.0(2)	32.0	
Pb(2)	32(e)	II	22370(1) ^a	22370(11)	22370(1)	76(10)	76(10)	76(10)	-10(12)	-10(12)	-10(12)	13.4(1)	14.0	
Pb(3)	32(e)	II	23989(12) ^a	23989(12)	23989(12)	334(11)	334(11)	334(11)	144(13)	144(13)	144(13)	17.5(2)	18.0	
O(5)	32(e)	II'	1721(11)	1721(11)	1721(11)	761(127)						26(4)	32.0	

^a Positional and anisotropic thermal parameters are given $\times 10^4$; exception: the positional coordinates of Pb(n) are given $\times 10^5$. Numbers in parentheses are the esd's in the units of the least significant digit given for the corresponding parameter. ^b The anisotropic temperature factor = $\exp[-2\pi^2/a^2(h^2U_{11} + k^2U_{22} + l^2U_{33} + 2hkU_{12} + 2hlU_{13} + 2klU_{23})]$. ^c Occupancy factors are given for the number of atoms or ions per unit cell. ^d $U_{iso} = (B_{iso}/8\pi^2)$.

ature (ca. 25 °C/h to 420 °C) and decreasing the pressure to 2×10^{-6} Torr. Finally the system was maintained at this state for 48 h. After the crystal had cooled to 14 °C, it was sealed in its capillary from the vacuum line by torch. Microscopic examination showed that it had become dark gray.

X-ray Data Collection. The cubic space group $Fd\bar{3}$ was used throughout this work. The space group was justified by the intensity inequality observed for hkl and khl reflections. ($Fd\bar{3}m$ appears to be more appropriate for faujasite (or zeolite Y) with its higher Si/Al ratio.) The unit cell constant at 21(1) °C, determined by least-squares refinement of 25 intense reflections for which $14^\circ < 2\theta < 24^\circ$, is $a = 25.238(5)$ Å. Molybdenum $K\alpha$ radiation ($\lambda_1 = 0.70930$, $\lambda_2 = 0.71359$ Å) was used for all experiments. The intensities of all lattice points for which $2\theta < 50^\circ$ were recorded. Of the 1421 reflections examined, only the 486 for which $I > 3\sigma(I)$ were used in subsequent structure determination. Absorption corrections ($\mu = 1.68$ mm⁻¹ and $\rho_{cal} = 2.60$ g cm⁻³)²⁴ were made empirically using a ψ scan. The calculated transmission coefficients ranged from 0.873 to 0.941. This correction caused the final R_1 and R_2 indices to decrease from 0.081 and 0.075 to 0.080 and 0.070, respectively. Other details are the same as previously reported.²⁵

Structure Determination. Full-matrix least-squares refinement was initiated with the framework atoms [Si, Al, O(1), O(2), O(3), and O(4)] of dehydrated Ca, Mg-X.²⁶ Isotropic refinement of the framework atoms converged to an R_1 index, $\sum|F_o - |F_c||/\sum F_o$, of 0.56 and a weighted R_2 index, $(\sum w(F_o - |F_c|)^2/\sum wF_o^2)^{1/2}$, of 0.63.

A difference Fourier function revealed two large peaks, at (0.07, 0.07, 0.07) and (0.24, 0.24, 0.24) with heights of 8.7 and 6.2 e Å⁻³, respectively. Isotropic refinement including them as Pb²⁺ ions at Pb(1) and Pb(3) converged to $R_1 = 0.25$ and $R_2 = 0.23$. From a subsequent difference Fourier function, a peak of height 7.1 e Å⁻³ was found at (0.166, 0.166, 0.166), which was refined as O(5). Isotropic refinement including this peak as O(5) converged to $R_1 = 0.23$ and $R_2 = 0.21$. Pb(2) was refining as 30 lead ions, but with a large thermal parameter of $B = 4.0$ Å², so it was split into Pb(2) at (0.24, 0.24, 0.24) and Pb(3) at (0.22, 0.22, 0.22). Isotropic refinement converged quickly to $R_1 = 0.12$ and $R_2 = 0.10$.

The occupancy numbers of Pb(1), Pb(2), Pb(3), and O(5) were revised, by the assumption of stoichiometry and by the requirement that the structure be plausible, to the values shown for the nonframework positions in the fixed-occupancy column of Table 1. Final isotropic refinement of the framework atoms and the nonframework oxygen at O(5), and anisotropic refinement of the Pb²⁺ ions at Pb(1), Pb(2), and Pb(3), converged to $R_1 = 0.080$ and $R_2 = 0.070$.

TABLE 2: Selected Interatomic Distances (Å) and Angles (deg)^a

Si-O(1)	1.58(2)	O(1)-Si-O(2)	112(1)
Si-O(2)	1.64(2)	O(1)-Si-O(3)	114(1)
Si-O(3)	1.61(2)	O(1)-Si-O(4)	112(1)
Si-O(4)	1.63(2)	O(2)-Si-O(3)	105(1)
average	1.62	O(2)-Si-O(4)	102(1)
Al-O(1)	1.67(2)	O(3)-Si-O(4)	111(1)
Al-O(2)	1.78(2)	O(1)-Al-O(2)	112(1)
Al-O(3)	1.74(2)	O(1)-Al-O(3)	112(1)
Al-O(4)	1.71(2)	O(1)-Al-O(4)	116(1)
average	1.72	O(2)-Al-O(3)	101(1)
Pb(1)-O(3)	2.67(2)	O(2)-Al-O(4)	101(1)
Pb(1)-O(5)	2.59(3)	O(3)-Al-O(4)	111(1)
Pb(2)-O(2)	2.32(2)		
Pb(2)-O(4)	2.77(2)	Si-O(1)-Al	142(1)
Pb(2)-O(5)	2.24(2)	Si-O(2)-Al	147(1)
Pb(3)-O(2)	2.54(2)	Si-O(3)-Al	143(1)
Pb(3)-O(4)	2.83(2)	Si-O(4)-Al	143(1)
Pb(3)-O(5)	2.95(2)		
O(5)-O(5)	3.39(3)	O(3)-Pb(1)-O(3)	98.3(6)
Pb(1)-Pb(1)	3.89(1)	O(5)-Pb(1)-O(5)	81.9(6)
		O(3)-Pb(1)-O(5)	90.5(4)
Pb(1)-O(5)-Pb(1)	97.6(7)	O(2)-Pb(2)-O(2)	117.2(7)
Pb(1)-O(5)-Pb(2)	119.7(7)	O(2)-Pb(2)-O(5)	80.2(6)
Pb(1)-O(5)-Pb(3)	119.7(7)	O(2)-Pb(3)-O(2)	102.5(6)
		O(2)-Pb(3)-O(5)	64.2(5)

^a The numbers in parentheses are the esd's in the units of the least significant digit given for the corresponding parameter.

The goodness-of-fit, $(\sum w(F_o - |F_c|)^2/(m-s))^{1/2}$, is 2.9; m (486) is the number of observations, and s (36) is the number of variables in least squares. All shifts in the final cycles of refinement were less than 0.01% of their corresponding standard deviations. A subsequent difference Fourier function revealed 23 small peaks of height 1.2–2.8 e Å⁻³. The largest (2.8(7) e Å⁻³) was located at the center of the sodalite cage. Least-squares refinement of this peak with the thermal parameter fixed at $B_{iso} = 2.7$ lowered R_2 only 0.000 68 and showed occupancies of 3.0(10) O²⁻ or 0.28(9) Pb²⁺. As oxide, this peak is too close to O(5) (2.06 Å) and so was not considered further. The second (0.061, 0.094, 0.058, height = 2.5(2) e Å⁻³) and third largest peaks (0.253, 0.271, 0.278, height = 1.6(2) e Å⁻³) were not stable in least squares.

Atomic scattering factors for Si, Al, O⁻, and Pb²⁺ were used.²⁵ All scattering factors were modified to account for anomalous dispersion.²⁵ The final structural parameters and selected interatomic distances and angles are presented in Tables 1 and 2, respectively.

Discussion

Zeolite X is a synthetic counterpart of the naturally occurring mineral faujasite. The truncated cubo-octahedron, a 14-hedron

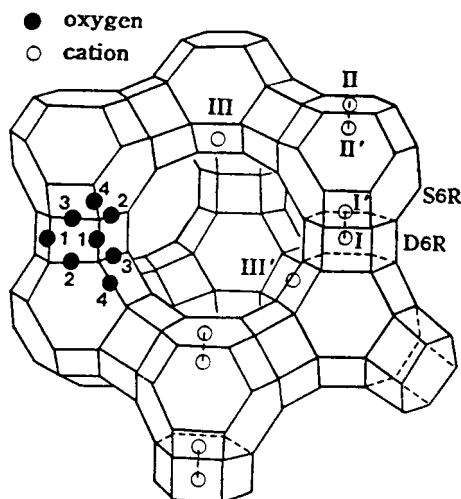


Figure 1. Stylized drawing of the framework structure of zeolite X. Near the center of each line segment is an oxygen atom. The different oxygen atoms are indicated by the numbers 1–4. Silicon and aluminum atoms alternate at the tetrahedral intersections, except that Si substitutes for Al at about 4% of the Al positions. Extraframework cation positions are labeled with Roman numerals.

with 24 vertices also known as the sodalite cavity or β cage, may be viewed as the principal building block of the aluminosilicate framework of the zeolite. These β cages are connected tetrahedrally at six-rings by bridging oxygens (see Figure 1) to give double six-rings (D6R's, hexagonal prisms) and concomitantly to give an interconnected set of even larger cavities (supercages) accessible in three dimensions through 12-ring (24-membered) windows. The Si and Al atoms occupy the vertices of these polyhedra. The oxygen atoms lie approximately half-way between each pair of Si and Al atoms but are displaced from those points to give near tetrahedral angles about Si and Al.

Exchangeable cations, which balance the negative charge of the aluminosilicate framework, are found within the zeolite's cavities. They are usually found at the following sites shown in Figure 1: site I at the center of a D6R, site I' in the sodalite (β) cavity on the opposite side of one of the D6R's 6-rings from site I, II' inside the sodalite cavity near a single 6-ring (S6R, shared by a β and a supercage) entrance to the supercage, II in the supercage adjacent to a S6R, III in the supercage opposite a 4-ring between two 12-rings, and III' somewhat off III (off the 2-fold axis).^{27,28}

The ordering of the Al and Si atoms in the lattice, justifying the choice of space group $Fd\bar{3}$, is confirmed by the average values of the Si–O (1.62 Å) and Al–O (1.72 Å) distances. These averaged bond distances are only somewhat sensitive to ion exchange and dehydration, but individual Si–O and Al–O distances can show marked variations (see Table 2). In this structure, differences are all due to the uneven coordination of framework oxygens by Pb cations: the O(1) oxygen has no contacts with cations at all, but O(2) associates strongly with either a Pb⁴⁺ ion at Pb(2) or a Pb²⁺ ion at Pb(3). (Pb²⁺ to O(3) and O(4) distances are longer.) For this reason, the Si–O(2) and Al–O(2) distances are perhaps the longest (see Table 2).

In this work, 64 Pbⁿ⁺ ions, 18 more than the 46 Pb²⁺ ions needed to balance the framework charge (a 39% overexchange), are found per unit cell. The degree of overexchange is sensitive to the pH of the exchange solution and would be less at lower pH's.

Thirty-two Pb²⁺ ions at Pb(1) are found at site I'. Each is recessed *ca.* 1.32(3) Å into the sodalite unit from the three O(3)

oxygen plane and is coordinated at 2.67(2) Å to those three oxygens, O(3), and at 2.59(3) Å to three nonframework oxygens, O(5) (see Figure 2). The near octahedral angles at Pb(1) are given in Table 2.

Eighteen Pb²⁺ ions at Pb(3) are found at site II (see Figures 2 and 3). Each is recessed *ca.* 1.12(2) Å into the supercage from the three O(2) oxygen plane of its S6R and coordinates to these three O(2)'s at 2.54(2) Å and to an O(5) at 2.95(2) Å. The O(2)–Pb(3)–O(2) angle is 102.5(6)°. Geometry involving O(2) is likely to be imprecise because only an average O(2) position has been determined; some O(2)'s bind to Pb⁴⁺ (*vide infra*) and others to Pb²⁺.

Finally, 14 lead ions at Pb(2) are found at site II. Each is recessed only 0.40(2) Å into the supercage from the three O(2) oxygen plane and coordinates near trigonally to these three O(2) oxygens of its S6R at 2.32(2) Å and axially to one nonframework oxygen, O(5) at 2.24(2) Å (see Figure 2). These very short Pb–O distances observed between Pb(2) and framework and nonframework oxygens indicate that Pb²⁺ has been oxidized to Pb⁴⁺. Such short Pb–O bonding distances were not seen in Pb₅₃(OH)₁₉–X.⁵ This suggests that elevated temperatures are required to oxidize Pb²⁺ to Pb⁴⁺. The smaller deviation of Pb(2) (0.40(2) Å) from its three O(2) oxygen plane, as compared to 1.12(2) Å for Pb(3), is consistent with the proposed oxidation of Pb²⁺ to Pb⁴⁺. Also its smaller thermal parameters, as compared to those of Pb(1) and Pb(3), are consistent with Pb(2) being extremely tightly bound to its four framework oxygens. Such short Pb⁴⁺–O bonding distances are found in several compounds. Ba₂PbO₄²⁹ has Pb–O distances of 2.15 and 2.07 Å. Pb⁴⁺ is distorted octahedral in β -PbO₂³⁰ (Pb–O = 2.15 and 2.17 Å). In the structure of Pb₉(OH)₈–(H₂O)₃–A⁴, Pb⁴⁺ coordinates to three framework oxygens (Pb–O = 2.17 Å) and to two nonframework oxygens (Pb–O = 2.2 Å). The O(2)–Pb(2)–O(2) angle is 116(1)°, nearly trigonal planar.

All four ligand oxygens about each ion at Pb(2) and Pb(3) lie on the same side of the lead ion (on the same side of a plane at lead drawn perpendicular to a 3-fold axis). Eighteen of the 32 O(5) oxide ions per unit cell within the sodalite units coordinate to four Pb²⁺ ions in a distorted tetrahedral manner. The remaining 14 coordinate to three Pb²⁺ ions and to one Pb⁴⁺ (see Figures 2 and 4 and Table 2).

Each sodalite cage is completely filled by a Pb₄O₄ cluster with a tetrahedrally distorted cubane structure with O²⁻ and Pb²⁺ alternating (see Figures 2 and 4). This neutral Pb₄O₄ cluster may be viewed as the core of the [(Pb²⁺)₆(Pb⁴⁺)₂(O²⁻)₄]¹²⁺ (six per unit cell) and [(Pb²⁺)₇Pb⁴⁺(O²⁻)₄]¹⁰⁺ (two per unit cell) clusters.

Nardin *et al.* observed that the sodalite cage is fully occupied by the lead hydroxide cluster [Pb₄(OH)₄]⁴⁺ in the structure of Pb₅₃(OH)₁₉–X⁵ dehydrated at 150 °C. The structures of Pb₂O₂ and Pb₄O₄ have been studied by using matrix isolation vibrational spectroscopy;³¹ that Pb₄O₄ cluster is thought to have a cubane structure with atomic distances similar to those found here.

It is expected that a lone pair of electrons extends from each Pb²⁺ ion at Pb(3) into the supercage. Pb²⁺ exhibits this behavior in some of its compounds, leaving a large solid angle for a nonbonding electron pair.^{32–38} From the environment about Pb(3), ample solid angle is available at this axial site on the zeolite's 3-fold axis. An axial placement had not been seen before for this electron pair in the chemistry of Pb²⁺; it is a consequence of the severe distortion of the trigonal pyramidal coordination about this Pb²⁺ ion, which occurs because Pb²⁺ is too large to lie in the plane of its six-ring. This pair of electrons

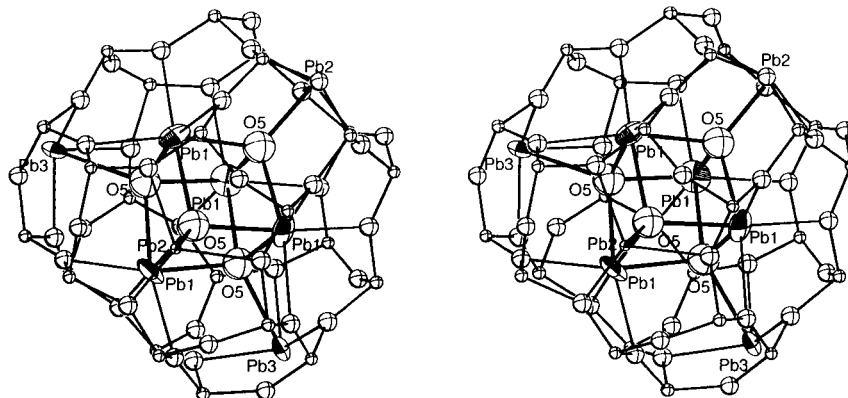


Figure 2. Stereoview of a sodalite cavity in dehydrated $\text{Pb}_{64}\text{O}_{32}\text{-X}$. Four Pb^{2+} ions at Pb(1) (site I'), two Pb^{4+} ions at Pb(2) (site II), two Pb^{2+} ions at Pb(3) (site II), and four O^{2-} ions at O(5) (site II') are shown. Ellipsoids of 20% probability are used.

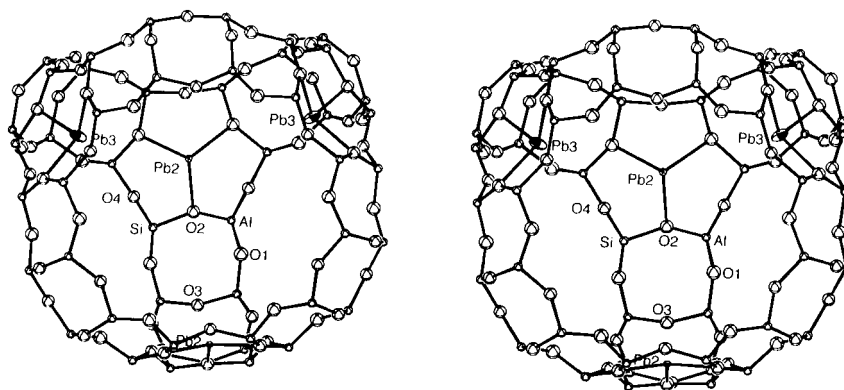


Figure 3. Stereoview of a supercage in dehydrated $\text{Pb}_{64}\text{O}_{32}\text{-X}$. Two Pb^{4+} ions at Pb(2) (site II) and two Pb^{2+} ions at Pb(3) (site II) are shown. About 75% of supercages per unit cell may have this arrangement. The remaining 25% of the supercages may have only one Pb^{4+} ion at Pb(2) and three Pb^{2+} ions at Pb(3). Ellipsoids of 20% probability are shown.

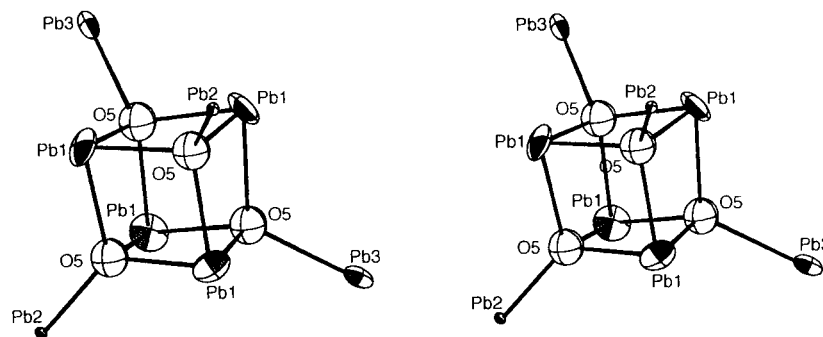


Figure 4. $[(\text{Pb}^{2+})_6(\text{Pb}^{4+})_2(\text{O}^{2-})_4]^{12+}$ cluster within, and extending out of, the sodalite cavity. A neutral Pb_4O_4 cluster is at its core.

may be relatively easily attacked, by H^+ for example, and lost to form Pb^{4+} .

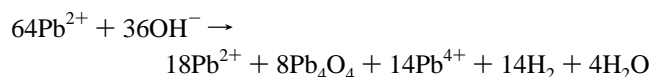
In this work, the Pb(1)–Pb(1) distance is *ca.* 3.89(1) Å, indicating that Pb–Pb interactions are not strong in Pb_4O_4 . In the $\text{Pb}_4(\text{OH})_4^{4+}$ and $\text{Pb}_6\text{O}(\text{OH})_6^{4+}$ clusters, the Pb–Pb distances are *ca.* 3.8 Å.^{10,14,39} In PbO–SiO₂ glasses⁴⁰ Pb–Pb distances are *ca.* 3.9 Å; in PbO–PbX₂ glasses (X = F, Cl),^{41–43} they are *ca.* 3.6 Å.

If the wash step is omitted in the preparation of the crystal, *ca.* nine additional Pb^{2+} ions are found in the large cavity at III' sites (four at (0.0549, 0.0534, 0.403) and five at (0.0156, 0.0172, 0.4134)). A shorter wash step, perhaps 30 min, seems sufficient to remove these nine Pb^{2+} ions.

When zeolite A is ion-exchanged with aqueous lead nitrate at pH = 4.3, 5% overexchange (6.3 Pb^{2+} ions per unit cell) is found.⁴ With aqueous lead acetate (pH = 6.0), 50% overexchange (9.0 Pb^{2+} ions per unit cell) occurs.^{3,4} With zeolite X, using lead nitrate, the extent of overexchange is 23%.⁵

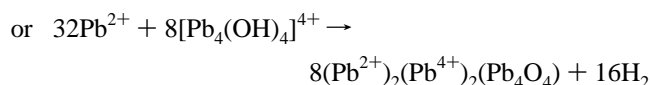
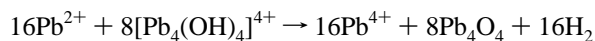
The greater degree of overexchange (39%) found in this work indicates that the extent of Pb^{2+} exchange into zeolite X increases with the pH of the exchange solution, as it did with zeolite A. This is affirmed in detail by the measurement of the $\text{Na}^+/\text{Pb}^{2+}$ exchange isotherms at pH = 5.0, 6.0, and 7.0 in zeolite X.⁴⁴

The standard oxidation potential for the formation of Pb^{4+} in basic solution is *ca.* –0.28 V. However, the reaction might reasonably have had a positive potential within the zeolite at dehydration temperature (420 °C) and a low H_2 pressure ($<2 \times 10^{-6}$ Torr), as proposed for zeolite A.⁴ In this structure, Pb^{4+} formed upon evacuation at elevated temperatures by a reaction which may be written (unreduced, with reference to one unit cell) as

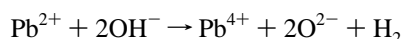


Approximately this amount of hydrogen gas was evolved when a powder sample of similar composition was heated.⁴⁵

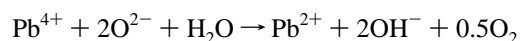
A simpler stoichiometry can be envisioned for zeolite X with a Si/Al ratio of 1.00. Na₉₆Si₉₆Al₉₆O₃₈₄, upon ion exchange with Pb²⁺ at pH = 6.0, might also accept 64 Pb²⁺ ions as in this work, corresponding to the complete exchange of [Pb₄(OH)₄]⁴⁺ into the sodalite cavities and of Pb²⁺ otherwise. The net reaction per unit cell upon heating could be expressed as follows:



The net reaction, oversimplified, could be written as



The dehydrated zeolite may be expected to react with water as follows:



No kinetic impediment to this reaction is seen because the Pb⁴⁺ ions are inadequately coordinated and easily accessible (see Figure 3). If the latter reaction proceeds at a reasonable rate, the processes of “dehydration” and “rehydration” might be used cyclically for the thermal decomposition of water.

The dehydrated zeolite might also be used as the anode in a voltaic cell. It would have the advantage of being easily regenerated by heating without requiring the physical movement (cyclic dissolution and deposition) of lead ions.

Because Pb₄O₄ is noncentric, and because PbO is a semiconductor, pronounced nonlinear optical behavior (such as frequency doubling) is likely.

In summary, site I' is fully occupied by 32 Pb²⁺ ions. These combine with 32 oxide ions to give neutral Pb₄O₄ clusters, one per sodalite unit, with a distorted cubane structure. Site II, along the 3-fold axis, is also fully occupied by 32 Pb ions; 18 Pb²⁺ and 14 Pb⁴⁺. Sites I and III are empty. Fourteen Pb²⁺ ions per unit cell have been oxidized to Pb⁴⁺ at elevated temperature. The range of Pb–O distances in this structure is 2.24–2.95 Å. A 39% overexchange (64 Pb's per unit cell) has occurred; this is a consequence of the pH of the exchange solution used.

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Supporting Information Available: Table of observed and calculated structure factors with estimated standard deviations, for the fully dehydrated structure, (Pb⁴⁺)₁₄(Pb²⁺)₁₈(Pb₄O₄)₈Si₁₀₀-

Al₉₂O₃₈₄ (14 pages). Ordering information is given on any current masthead page.

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