

# Crystal structure of $\text{Pb}_{44}^{2+}\text{Pb}_{5}^{4+}\text{Tl}_{18}^{+}\text{O}_{17}^{2-}-\text{Si}_{100}\text{Al}_{92}\text{O}_{384}$ , zeolite X exchanged with $\text{Pb}^{2+}$ and $\text{Tl}^{+}$ and dehydrated, containing $\text{Pb}_4\text{O}_4(\text{Pb}^{2+}, \text{Pb}^{4+} \text{ mixed})_4$ clusters

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## Abstract

A single crystal of zeolite X was ion exchanged using a mixed aqueous solution, equinormal in  $\text{Pb}^{2+}$  and  $\text{Tl}^{+}$ , with a total concentration of 0.05 M. It was then vacuum dehydrated at 380°C and  $2 \times 10^{-6}$  Torr, and its structure was determined by X-ray diffraction techniques in the cubic space group  $Fd\bar{3}$  at 21°C ( $a = 25.119(6)$  Å). The structure, of formula  $\text{Pb}_{44}^{2+}\text{Pb}_{5}^{4+}\text{Tl}_{18}^{+}\text{O}_{17}^{2-}-\text{Si}_{100}\text{Al}_{92}\text{O}_{384}$  per unit cell, was refined to the final error indices  $R_1 = 0.057$  and  $R_2 = 0.055$  with 475 reflections for which  $I > 3\sigma(I)$ . The reaction that occurred upon evacuation at elevated temperature may be written, per unit cell, as  $34\text{Pb}^{2+} + 24\text{OH}^- \rightarrow 4.25[\text{Pb}_4\text{O}_4(\text{Pb}_{12/17}^{2+}, \text{Pb}_{5/17}^{4+})_4]^{176/17+} + 5\text{H}_2 + 7\text{H}_2\text{O}$ . Lead ions occupy three nonequivalent sites. Five lead ions at site II are identified as  $\text{Pb}^{4+}$  by their coordination geometry: each is nearly in a six-ring plane where it coordinates to three framework oxygen atoms at 2.23(2) Å and also to a nonframework oxygen at 2.11(7) Å. There are also 12  $\text{Pb}^{2+}$  ions occupying site II: each is 2.45(2) Å from three framework oxygen atoms and 2.78(7) Å from a nonframework oxygen. About 53% of the sodalite cages are filled by a  $\text{Pb}_4\text{O}_4(\text{Pb}^{2+}, \text{Pb}^{4+} \text{ mixed})_4$  cluster whose neutral  $\text{Pb}_4\text{O}_4$  core is nearly a cube with  $\text{Pb}^{2+}$  and  $\text{O}^{2-}$  ions alternating. The four  $\text{Pb}^{2+}$  ions in the core are at site I', where each is 2.594(14) Å from three framework oxygen atoms and 2.62(6) Å from three nonframework oxygen atoms. There are 18  $\text{Tl}^{+}$  ions located at two nonequivalent sites: 15 complete the filling of site II (each is 2.708(14) Å from three framework oxygen atoms), and the remaining three are at III' (each is 2.52(8) Å from one framework oxygen and 3.12(9) Å from another). Upon dehydration, the zeolite retains only those nonframework oxygen atoms that can be accommodated in  $\text{Pb}_8\text{O}_4^{n+}$  clusters. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Dehydrated; Ion exchange; Lead;  $\text{Pb}_8\text{O}_4^{n+}$ ; Structure; Thallium; Zeolite X

## 1. Introduction

Wiers et al. [1] suggested that  $\text{H}^+$ -exchange may be responsible for the differing pH values of aqueous slurries (that is of the very dilute solution after

equilibrium between a zeolite sample and water) of Na-A and Ca-A. This suggests further that the extent of exchange might in some cases depend on pH if flow methods are used.

Hertzenberg and Sherry [2] observed a small overexchange of  $\text{Pb}^{2+}$  into zeolite 4A from 0.1 M  $\text{Pb}(\text{NO}_3)_2$ . The crystal structure of  $\text{Pb}_9\text{O}(\text{OH})_4$ -A, zeolite 4A exchanged with  $\text{Pb}^{2+}$  at a

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higher pH, 6.0, (and evacuated at 26°C) showed that a much higher degree of overexchange of  $\text{Pb}^{2+}$  (50%) had occurred [3]. The structure of Na–A ion exchanged with ultrapure  $\text{Pb}^{2+}$  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  $\text{Pb}^{2+}$  per unit cell had occurred, due presumably to cation hydrolysis [4]. Also, it appeared that just one of the  $\text{Pb}^{2+}$  ions per 12.3 Å pseudocell had been oxidized to  $\text{Pb}^{4+}$ . On the other hand, if ion exchange is done by flow methods with 0.1 M  $\text{Pb}(\text{NO}_3)_2$  (pH=4.3), only fractionally more than six  $\text{Pb}^{2+}$  ions (the stoichiometric number) exchange into the zeolite [2,4].

$[\text{Pb}_4(\text{OH})_4]^{4+}$  clusters have been reported in the sodalite cages of  $\text{Pb}^{2+}$ -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  $\text{Pb}^{2+}$  ions migrate from the sodalite cages into the large cavities [5].

More recently, the crystal structure of fully dehydrated  $\text{Pb}^{2+}$ -exchanged zeolite X,  $\text{Pb}_{64}\text{O}_{32}\text{-Si}_{100}\text{Al}_{92}\text{O}_{384}$ , was determined by X-ray diffraction techniques [6]. In that work, a single crystal of zeolite X was 39%-overexchanged after treatment with aqueous  $\text{Pb}^{2+}$  at pH 6.0 followed by brief washing with water. (This washing (minutes) decreased the  $\text{Pb}^{2+}$  content of the zeolite and eliminated some low occupancy Pb positions from the resulting crystal structure; a more extensive washing (hours) had no further noticeable effects.) Substantial amounts of  $\text{Pb}^{4+}$  had formed upon evacuation at elevated temperature.

Lead hydrolyzes extensively in aqueous solution [7–10]. The compositions of aqueous equilibrium mixtures have been investigated by a variety of techniques such as potentiometric titration [11], vibrational analysis [11],  $^{207}\text{Pb}$  NMR [12], Raman spectroscopy [13], and theoretical calculation [14]. The complexation of  $\text{Pb}^{2+}$  by hydroxide has been studied in molten  $(\text{K},\text{Na})\text{NO}_3$  at 280°C by various techniques [15].

The structure of  $\text{Tl}_{92}\text{-Si}_{100}\text{Al}_{92}\text{O}_{384}$ , fully dehydrated  $\text{Tl}_{92}\text{-X}$ , has been determined by single-crystal X-ray diffraction [16]. In that structure, 92  $\text{Tl}^+$  ions occupy four nonequivalent sites: 32 are at site I', another 32 are at site II, 16 are at

site III', and the remaining 12 are at another site III'.

This work was done to investigate the effect of  $\text{Tl}^+$  on the extent of  $\text{Pb}^{2+}$  overexchange, and on the subsequent formation of  $\text{Pb}^{4+}$ ,  $\text{H}_2(\text{g})$ , and lead oxide clusters.  $\text{Tl}^+$  dilutes the  $\text{Pb}^{2+}$  content of the initially exchanged zeolite, and may itself be oxidized and/or participate in clusters.

## 2. 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 [17]. One of these, a colorless octahedron about 0.2 mm in cross-section, was lodged in a fine Pyrex capillary. Ion exchange was accomplished by flow methods using an exchange solution in which the molar ratio  $\text{Pb}(\text{O}_2\text{CCH}_3)_2:\text{TlNO}_3$  was 1:2, with a total concentration of 0.05 M; pH=6.0. The exchange solution was allowed to flow past the crystal at a velocity of approximately  $0.5 \text{ mm s}^{-1}$  for 3 days at 17°C. The crystal was washed by continuing this procedure using distilled water for 1 h. The crystal in its finely drawn Pyrex capillary was attached to a vacuum system and was cautiously dehydrated by gradually increasing its temperature (ca.  $25^\circ\text{C h}^{-1}$  to 380°C) at a constant pressure of  $2 \times 10^{-6}$  Torr. Finally, these conditions were maintained for 48 h. After the crystal had cooled to room temperature, it was sealed in its capillary from the vacuum line by torch. Microscopic examination showed that it had become dark brown.

### 2.1. X-ray data collection

The cubic space group  $Fd\bar{3}$  was used throughout this work. This space group was justified by the intensity inequality observed for  $hkl$  and  $khl$  reflections. Molybdenum  $\text{K}\alpha$  radiation was used for all experiments ( $\text{K}\alpha_1$ ,  $\lambda=0.70930 \text{ \AA}$ ;  $\text{K}\alpha_2$ ,  $\lambda=0.71359 \text{ \AA}$ ). The unit cell constant at 21(1)°C, determined by least-squares refinement of 24 relatively intense reflections for which  $18 < 2\theta < 23^\circ$ , is  $a=25.119(6) \text{ \AA}$ . All unique reflections in the positive octant of an F-centered unit cell for which  $2\theta < 60^\circ$ ,  $l > h$ , and  $k > h$  were recorded. Of the

1436 unique reflections examined, only the 475 for which  $I > 3\sigma(I)$  were used in subsequent structure determination and refinement. A spherical absorption correction ( $\mu R = 1.73$  and  $\rho_{\text{cal}} = 2.68 \text{ g cm}^{-3}$ ) [18] was attempted. The calculated transmission coefficients ranged from 0.101 to 0.121. This correction had little effect on the final  $R$  indices. Other details are the same as previously reported [19].

## 2.2. 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  $\text{Pb}_{64}\text{O}_{32}\text{-X}$  [6]. Isotropic refinement of the framework atoms converged to an  $R_1$  index ( $\sum |F_o - F_c| / \sum F_o$ ) of 0.53 and a weighted  $R_2$  index [ $\sum w(F_o - F_c)^2 / \sum wF_o^2$ ]<sup>1/2</sup> of 0.63.

A difference Fourier function revealed two large peaks at (0.072, 0.072, 0.072) and (0.241, 0.241, 0.241) with heights of  $11 \text{ e}^- \text{ \AA}^{-3}$  and  $5 \text{ e}^- \text{ \AA}^{-3}$  respectively. Isotropic refinement including them as  $\text{Pb}^{2+}$  ions at Pb(1) and Pb(3) converged to  $R_1 = 0.16$  and  $R_2 = 0.15$ . From the next difference Fourier function, a peak of height  $19 \text{ e}^- \text{ \AA}^{-3}$  was found at (0.225, 0.225, 0.225). Isotropic refinement including this peak as Pb(2) converged to  $R_1 = 0.09$  and  $R_2 = 0.08$ . On a subsequent difference Fourier function, a peak of height  $4.3 \text{ e}^- \text{ \AA}^{-3}$  was found at (0.256, 0.256, 0.256). Isotropic refinement including this peak as Tl(1) converged to  $R_1 = 0.067$  and  $R_2 = 0.064$ . From the next difference Fourier function, two peaks of height  $2.1 \text{ e}^- \text{ \AA}^{-3}$  and  $1.1 \text{ e}^- \text{ \AA}^{-3}$  were found at (0.065, 0.064, 0.410) and (0.176, 0.176, 0.176) respectively. Isotropic refinement including these peaks as Tl(2) and O(5) converged to  $R_1 = 0.066$  and  $R_2 = 0.057$ .

In the above, it was not difficult to distinguish  $\text{Pb}^{2+}$ ,  $\text{Pb}^{4+}$  and  $\text{Tl}^+$  ions for several reasons. Firstly, their ionic radii are quite different:  $\text{Pb}^{2+} = 1.20 \text{ \AA}$ ,  $\text{Pb}^{4+} = 0.84 \text{ \AA}$  and  $\text{Tl}^+ = 1.47 \text{ \AA}$ . Moreover, the approach distances between those ions and zeolite oxygen ions in dehydrated  $\text{Tl}_{92}\text{-X}$  [16] and  $\text{Pb}_{64}\text{O}_{32}\text{-X}$  [6] are known and are indicative. Secondly, because of their differing charges, the requirement that they sum to  $92+$  per unit cell does not allow the major positions to

refine to acceptable occupancies with an alternative assignment of ionic identities.

The occupancy numbers at Pb(1), Pb(2), Pb(3), Tl(1), Tl(2), and O(5) were adjusted and fixed as given in the last column of Table 1 to establish apparent stoichiometry and electrical neutrality while maintaining crystallographic occupancy limits. Final isotropic refinement of the framework atoms and the nonframework ions Tl(2) and O(5), and anisotropic refinement of the cations at Pb(1), Pb(2), Pb(3), and Tl(1), converged to  $R_1 = 0.057$  and  $R_2 = 0.055$ .

The goodness-of-fit [ $\sum w(F_o - F_c)^2 / (m - s)$ ]<sup>1/2</sup> is 1.96;  $m$  (475) is the number of observations, and  $s$  (43) is the number of variables in least squares. All shifts in the final cycles of least-squares refinement were less than 0.01% of their corresponding standard deviations.

The final difference Fourier function revealed five small peaks of height 1.3 to  $2.7 \text{ e}^- \text{ \AA}^{-3}$ . The largest ( $2.7(2) \text{ e}^- \text{ \AA}^{-3}$ ) was located at the center of the sodalite cage.

Least-squares refinement of this peak with the thermal parameter fixed at  $U_{\text{iso}} = 0.038 \text{ \AA}^2$  increased  $R_2$  by 0.002 and showed occupancies of  $1.6(9) \text{ O}^{2-}$  or  $0.1(1) \text{ Pb}^{2+}$ . As oxide, this peak was too close to O(5) ( $2.25 \text{ \AA}$ ) and so was not considered further.

The second- ( $0.093, 0.064, 0.057$ ; height,  $1.8(2) \text{ e}^- \text{ \AA}^{-3}$ ) and third-largest peaks ( $0.375, 0.093, 0.875$ ; height,  $1.5(2) \text{ e}^- \text{ \AA}^{-3}$ ) were not stable in least squares.

Atomic scattering factors for Si, Al,  $\text{O}^-$ ,  $\text{Pb}^{2+}$  and  $\text{Tl}^+$  were used [20]. All scattering factors were modified to account for anomalous dispersion [21]. The final structural parameters are presented in Table 1, and the selected interatomic distances and angles are presented in Table 2.

## 3. Discussion

Zeolite X is a synthetic counterpart of the naturally occurring mineral faujasite. The 14-hedron with 24 vertices known as the sodalite cavity or  $\beta$  cage may be viewed as the principal building block of the aluminosilicate framework of the zeolite (see Fig. 1). These  $\beta$  cages are connected tetrahe-

Table 1  
Positional, thermal<sup>a</sup>, and occupancy parameters

Atom	Wyckoff position	Site	x	y	z	$U_{11}^b$ or $U_{iso}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$	Occupancy <sup>c</sup>	
												varied	fixed
Si	96(g)		-533(3)	1255(3)	358(3)	95(16)						96	
Al	96(g)		-550(3)	366(3)	1240(3)	74(17)						96	
O(1)	96(g)		-1046(6)	-1(7)	1002(6)	249(43)						96	
O(2)	96(g)		-4(7)	-12(7)	1439(6)	195(40)						96	
O(3)	96(g)		-309(6)	777(6)	744(6)	141(39)						96	
O(4)	96(g)		-699(6)	713(6)	1807(6)	176(41)						96	
Pb(1)	32(e)	I	7216(5)	7216(5)	7216(5)	402(5)	402(5)	402(5)	-61(7)	-61(7)	-61(7)	31.2(3)	
Pb(2)	32(e)	II	22511(24)	22511(24)	22511(24)	52(24)	52(24)	52(24)	-66(26) <sup>d</sup>	66(26) <sup>d</sup>	-66(26) <sup>d</sup>	5.4(1)	
Pb(3)	32(e)	II	24033(8)	24033(8)	24033(8)	45(10)	45(10)	45(10)	-33(10)	-33(10)	-33(10)	11.8(1)	
Tl(1)	32(e)	II	25140(12)	25140(12)	25140(12)	312(9)	312(9)	312(9)	-41(13)	-41(13)	-41(13)	15.4(1)	
Tl(2)	96(g)	III'	582(31)	611(31)	4189(30)	1391(319)						4.4(4)	
O(5)	32(e)		1763(44)	1763(44)	1763(44)	2995(879)						12(6)	

<sup>a</sup> Positional and anisotropic thermal parameters are given  $\times 10^4$ , exception: the positions of Pb(*n*) and Tl(1) are given  $\times 10^5$ . Numbers in parentheses are the esds in the units of the least significant digit given for the corresponding parameter.

<sup>b</sup> The anisotropic temperature factor is given by  $\exp[(-2\pi^2/a^2)(h^2U_{11} + k^2U_{22} + l^2U_{33} + 2hkU_{12} + 2hlU_{13} + 2klU_{23})]$ .

<sup>c</sup> Occupancy factors are given as the number of atoms or ions per unit cell.

<sup>d</sup> This physically unacceptable value was increased by  $2\sigma$  in the preparation of the figures.

Table 2  
Selected interatomic distances (Å) and angles (deg)<sup>a</sup>

Si–O(1)	1.570(18)	O(1)–Si–O(2)	111.9(9)
Si–O(2)	1.661(19)	O(1)–Si–O(3)	110.5(9)
Si–O(3)	1.643(17)	O(1)–Si–O(4)	112.1(9)
Si–O(4)	1.635(18)	O(2)–Si–O(3)	104.9(8)
Al–O(1)	1.661(18)	O(2)–Si–O(4)	104.7(8)
Al–O(2)	1.741(18)	O(3)–Si–O(4)	112.3(9)
Al–O(3)	1.726(17)	O(1)–Al–O(2)	113.0(9)
Al–O(4)	1.710(18)	O(1)–Al–O(3)	109.6(9)
Pb(1)–O(3)	2.594(14)	O(1)–Al–O(4)	114.7(9)
Pb(1)–O(5)	2.62(6)	O(2)–Al–O(3)	104.9(8)
Pb(2)–O(2)	2.23(2)	O(3)–Al–O(4)	111.8(8)
Pb(2)–O(4)	2.88(2)	Si–O(1)–Al	146.8(11)
Pb(2)–O(5)	2.11(7)	Si–O(2)–Al	141.4(10)
Pb(3)–O(2)	2.45(2)	Si–O(3)–Al	138.0(10)
Pb(3)–O(5)	2.78(7)	Si–O(4)–Al	142.2(11)
Pb(3)–O(4)	2.94(2)		
Tl(1)–O(2)	2.708(14)	O(3)–Pb(1)–O(3)	94.3(5)
Tl(1)–O(4)	3.08(2)	O(5)–Pb(1)–O(5)	88.3(1)
Tl(2)–O(4)	2.52(8)	O(3)–Pb(1)–O(5)	89.5(4)
Tl(2)–O(1)	3.12(9)	O(2)–Pb(2)–O(2)	116.5(7)
O(5)–O(5)	3.65(8)	O(2)–Pb(2)–O(5)	79.0(3)
Pb(1)–Pb(1)	3.754(2)	O(2)–Pb(3)–O(2)	101.6(6)
		O(2)–Pb(3)–O(5)	63.0(1)
		O(2)–Tl(1)–O(2)	89.1(5)
		O(1)–Tl(2)–O(4)	54.0(2)
		Pb(1)–O(5)–Pb(1)	92.0(3)
		Pb(1)–O(5)–Pb(2)	124.0(3)

<sup>a</sup> The numbers in parentheses are the esds in the units of the least significant digit given for the corresponding parameter.

drally at six-rings (6Rs) by bridging oxygen atoms (six for each connection) 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. Each unit cell contains eight supercages, eight sodalite units, 16 D6Rs, 16 12-rings, and 32 single six-rings (S6Rs).

Exchangeable cations, which balance the negative charge of the aluminosilicate framework, are found within the zeolite cavities. They are usually found at the following sites (see Fig. 1): site I at the center of a D6R; site I' in the sodalite cavity on the opposite side of one of the D6R's six-rings

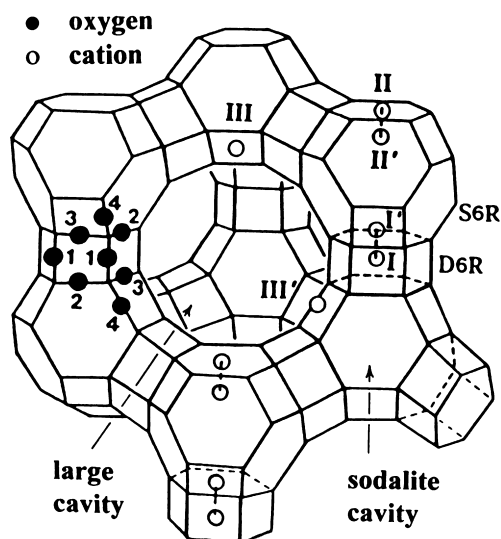


Fig. 1. Stylized drawing of the framework structure of zeolite X. Near the center of each line segment is an oxygen atom. The nonequivalent oxygen atoms are indicated by the numbers 1 to 4. Silicon and aluminum atoms alternate at the tetrahedral intersections, except that Si substitutes for Al at about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

from site I; II' inside the sodalite cavity near a S6R (shared by a  $\beta$  and a supercage); II in the supercage adjacent to a S6R; III in the supercage opposite a four-ring between two 12-rings; III' off the twofold axis, somewhat or substantially distant from III but otherwise near the inner walls of the supercage [22,23].

In this work, 49  $Pb^{n+}$  ions and 18  $Tl^{+}$  ions are found per unit cell. This demonstrates a strong selectivity of zeolite X for  $Pb^{2+}$  under the exchange conditions employed.

There are 32  $Pb^{2+}$  ions at Pb(1) filling site I'. Each extends ca. 1.38(1) Å into the sodalite unit from its three O(3) oxygen plane and coordinates at 2.594(14) Å to those three oxygen atoms (see Figs. 2 and 3 and Table 3). Of these 32, there are 17 coordinating to three O(5) nonframework oxygen atoms at 2.62(6) Å (see Fig. 3); the remaining 15 do not coordinate further (see Fig. 4). The positions of the former 17  $Pb^{2+}$  ions must, therefore, be somewhat different from the latter 15; crystallographic attempts to split this position into

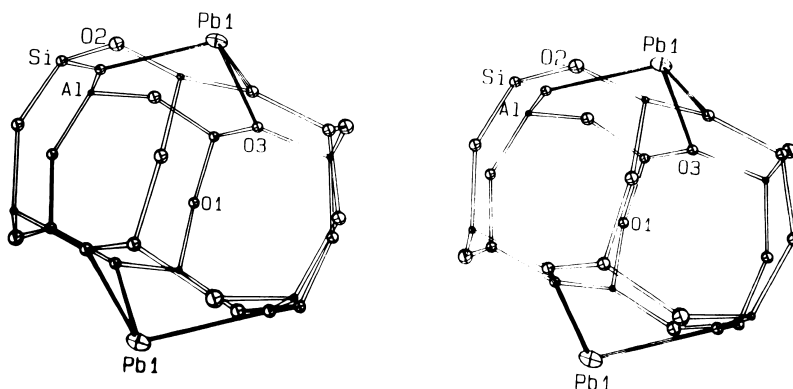


Fig. 2. Stereoview of a D6R. Each D6R hosts two  $\text{Pb}^{2+}$  ions at Pb(1) (site I'). Ellipsoids of 20% probability are used.

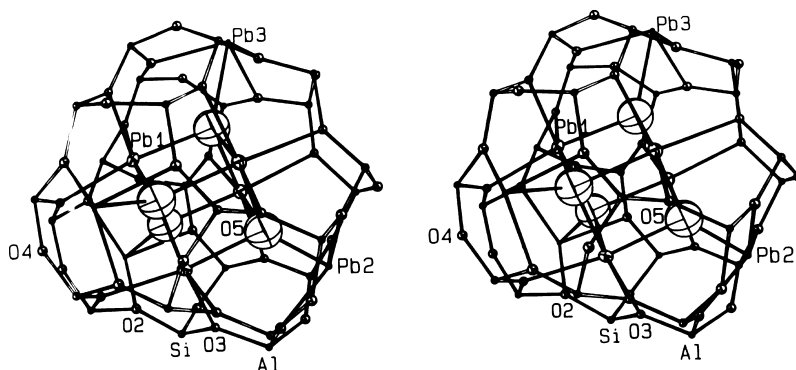


Fig. 3. Stereoview of most (4.25/8) of the sodalite cavities. Four  $\text{Pb}^{2+}$  ions at Pb(1) (site I') and four  $\text{O}^{2-}$  ions at O(5) are shown. At site II, one  $\text{Pb}^{4+}$  ion at Pb(2) and three  $\text{Pb}^{2+}$  ions at Pb(3) are shown. Ellipsoids of 20% probability are used.

Table 3  
Deviations of atoms (Å) from six-ring planes

At O(2) <sup>a</sup>	Tl(1)		1.59(1)
	Pb(2)	( $\text{Pb}^{4+}$ )	0.42(1)
	Pb(3)	( $\text{Pb}^{2+}$ )	1.10(1)
	O(5)		-1.69(7)
At O(3) <sup>b</sup>	Pb(1)	( $\text{Pb}^{2+}$ )	-1.38(1)

<sup>a</sup> A positive deviation indicates that the ion lies in the supercage.

<sup>b</sup> A negative deviation indicates that the ion lies in the sodalite cage.

two were unfortunately unsuccessful. The near octahedral angles at Pb(1) are given in Table 2.

At Pb(3) there are 12  $\text{Pb}^{2+}$  ions found at site II (see Fig. 3). Each extends ca. 1.10(1) Å into the

supercage from the three O(2) oxygen plane of its S6R. It coordinates to those three at 2.45(2) Å and to an O(5) at 2.78(7) Å; these distances are similar to those previously observed in  $\text{Pb}_{64}\text{O}_{32}\text{-X}$  [6], 2.95(2) Å and 2.54(2) Å respectively. The O(2)–Pb(3)–O(2) angle is 101.6(6)°.

The final five lead ions are at Pb(2), another site II (see Fig. 3). Each extends only 0.42(1) Å into the supercage from its three O(2) oxygen plane and, therefore, coordinates near-trigonally to those three oxygen atoms (Pb(2)–O(2) = 2.23(2) Å). Pb(2) also coordinates axially to one nonframework oxygen, O(5), at 2.11(7) Å. These short Pb–O distances had been observed previously in  $\text{Pb}_{64}\text{O}_{32}\text{-X}$  [6] (2.32(2) Å and 2.24(2) Å respectively) and indicate that  $\text{Pb}^{2+}$  has been oxidized to  $\text{Pb}^{4+}$ . For comparison, the sum of the  $\text{Pb}^{2+}$  and  $\text{O}^{2-}$  radii are 1.20 + 1.32 = 2.52 Å; that

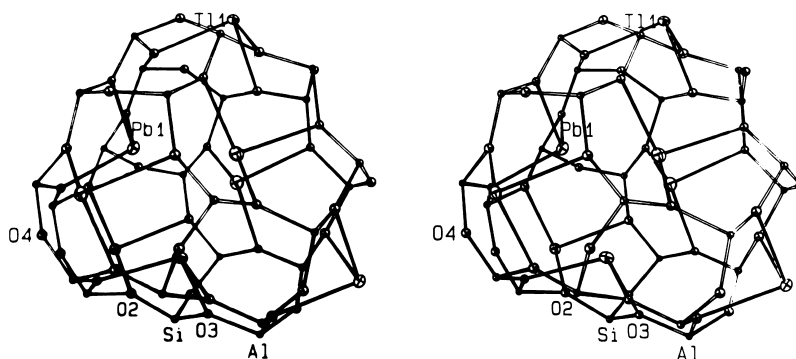


Fig. 4. Stereoview of the less common (3.75/8) sodalite cavity. Four  $\text{Pb}^{2+}$  ions at Pb(1) (site I') and four  $\text{Tl}^+$  ions at Tl(1) (site II) are shown. Ellipsoids of 20% probability are used.

for  $\text{Pb}^{4+}$  and  $\text{O}^{2-}$  is  $0.84 + 1.32 = 2.16 \text{ \AA}$  [24]. The smaller deviation of Pb(2) ( $0.42(1) \text{ \AA}$ ) from its three O(2) oxygen plane, compared with that for Pb(3) ( $1.10(1) \text{ \AA}$ ), is consistent with the proposed oxidation of  $\text{Pb}^{2+}$  to  $\text{Pb}^{4+}$ ; see Table 3.

These short  $\text{Pb}^{4+}$ –O bonding distances were not seen in  $\text{Pb}_{53}(\text{OH})_{19}\text{-X}$  [5]. This suggests that elevated temperatures are required to oxidize  $\text{Pb}^{2+}$  to  $\text{Pb}^{4+}$ . These short  $\text{Pb}^{4+}$ –O bonding distances are found in several compounds of  $\text{Pb}^{4+}$ .  $\text{Ba}_2\text{PbO}_4$  [25] has Pb–O distances of  $2.15 \text{ \AA}$  and  $2.07 \text{ \AA}$ .  $\text{Pb}^{4+}$  is distorted octahedral in  $\beta\text{-PbO}_2$  [26] (Pb–O =  $2.150(1) \text{ \AA}$  and  $2.1689(7) \text{ \AA}$ ). In  $\text{Pb}_9(\text{OH})_8(\text{H}_2\text{O})_3\text{-A}$  [4],  $\text{Pb}^{4+}$  coordinates to three framework oxygen atoms (Pb–O =  $2.17(2) \text{ \AA}$ ) and to two nonframework oxygen atoms (Pb–O =

$2.2(4) \text{ \AA}$ ). The O(2)–Pb(2)–O(2) angle is  $116.5(7)^\circ$ , nearly trigonal planar.

The geometry involving O(2) is likely to be imprecise because only an average O(2) position has been determined; some O(2) atoms bind to  $\text{Tl}^+$ , others to  $\text{Pb}^{4+}$ , and the remainder to  $\text{Pb}^{2+}$ .

All ligand oxygen atoms about each ion at Pb(2) and Pb(3) lie on the same side of the  $\text{Pb}^{n+}$  ion (on the same side of a plane at Pb drawn perpendicular to a threefold axis). All nonframework sodalite-unit oxides coordinate through S6Rs to the supercage Pb ions:  $\text{Pb}^{2+}$  or  $\text{Pb}^{4+}$ ; see Fig. 3.

At Tl(1) there are 15  $\text{Tl}^+$  ions occupying site II (see Figs. 4 and 5). Each extends ca.  $1.59(1) \text{ \AA}$  into the supercage from the three O(2) oxygen plane of its S6R and coordinates to those three

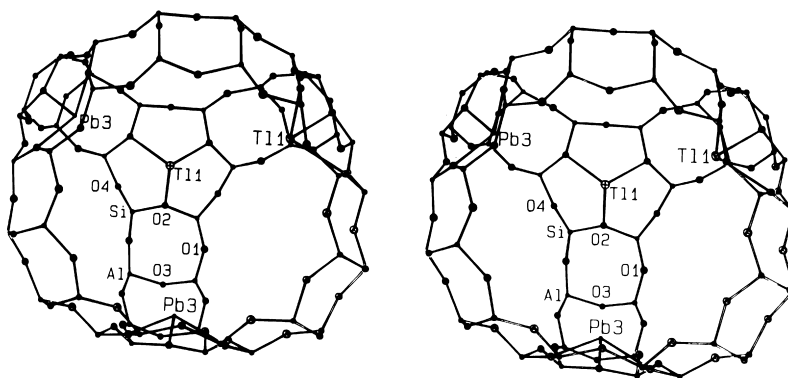


Fig. 5. Stereoview of the most common supercage. Two  $\text{Pb}^{2+}$  ions at Pb(3) and two  $\text{Tl}^+$  ions at Tl(1) are shown at site II. Ellipsoids of 20% probability are used.

O(2) atoms at 2.708(4) Å. For comparison, the distance between Tl<sup>+</sup> at site II and O(2) in dehydrated Tl<sub>92</sub>-X is 2.68(1) Å. The O(2)-Tl(1)-O(2) angle of 89.1(5)° observed here is very similar to that in Tl<sub>92</sub>-X [16], i.e. 89.7(5)°.

The final three Tl<sup>+</sup> ions at Tl(2) lie in 12-rings (III' sites). They bind strongly to one O(4) at 2.52(8) Å and to one O(1) at 3.12(9) Å (see Fig. 6). Such a short Tl-O bonding distance (2.38(4) Å) has been seen before in Tl<sub>92</sub>-X [16].

About 53% of the sodalite cages (4.25 of the eight per unit cell) are filled by a Pb<sub>4</sub>O<sub>4</sub>(Pb<sup>2+</sup>, Pb<sup>4+</sup> mixed)<sub>4</sub> cluster whose neutral Pb<sub>4</sub>O<sub>4</sub> core is nearly cubic with Pb<sup>2+</sup> and O<sup>2-</sup> ions alternating (Table 4). The four Pb<sup>2+</sup> ions in the core are at site I', where each is 2.594(14) Å from three framework oxygen atoms and

2.62(6) Å from three nonframework oxygen atoms. The remaining ca. 47% of the sodalite units (3.75 per unit cell) may have four Pb<sup>2+</sup> ions at Pb(1) in the sodalite cavity and four Tl<sup>+</sup> ions at Tl(1) outside the sodalite cavity, with each group of four ions arranged tetrahedrally (see Fig. 4) as in Pb<sub>4</sub>O<sub>4</sub>(Pb<sup>2+</sup>, Pb<sup>4+</sup> mixed)<sub>4</sub>, but without bridging oxygen atoms.

Nardin et al. [5] observed that the sodalite cages are fully occupied by lead hydroxide clusters [Pb<sub>4</sub>(OH)<sub>4</sub>]<sup>4+</sup> in the structure of Pb<sub>53</sub>(OH)<sub>19</sub>-X dehydrated at 150°C. The structures of the Pb<sub>2</sub>O<sub>2</sub> and Pb<sub>4</sub>O<sub>4</sub> clusters have been determined by matrix-isolation vibrational spectroscopy [27,28]; Pb<sub>4</sub>O<sub>4</sub> is thought to have a cubane structure with interatomic distances similar to those found here.

In this work, the Pb(1)-Pb(1) distance is

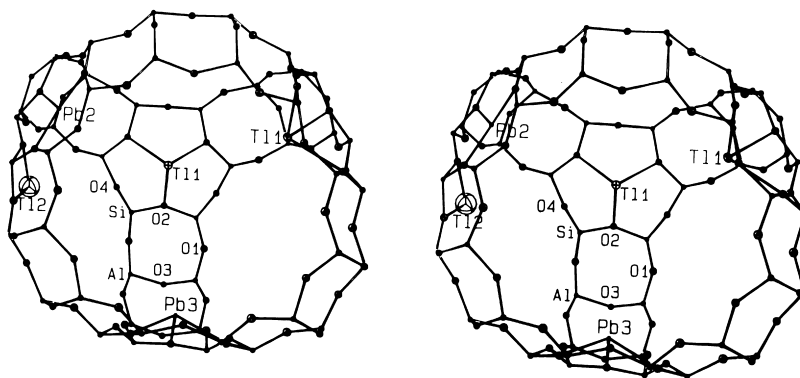


Fig. 6. Stereoview of a less common supercage. One Pb<sup>4+</sup> ion at Pb(2), one Pb<sup>2+</sup> ion at Pb(3), two Tl<sup>+</sup> ions at Tl(1), and one Tl<sup>+</sup> ion at Tl(2) are shown at site II. Ellipsoids of 20% probability are shown.

Table 4  
Inferred contents of the sodalite and supercages

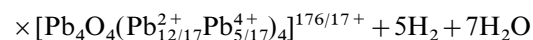
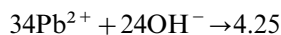
Ion	Sodalite cage			Supercage			
	with cluster		without cluster				
	43.7%	9.4%	46.9%	37.5%	25%	25%	12.5%
Pb(1) (Pb <sup>2+</sup> , site I')	4	4	4				
O(5)	4	4					
Pb(2) (Pb <sup>4+</sup> , site II)	1	2			1	1	1
Pb(3) (Pb <sup>2+</sup> , site II)	3	2		2	1	1	2
Tl(1) (site III)			4	2	2	2	1
Tl(2) (site III')						1	1



3.754(2) Å. 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 [11,15,27,28]. In  $\text{PbO-SiO}_2$  glasses [29,30], Pb–Pb distances are ca. 3.9 Å; in  $\text{PbO-PbX}_2$  glasses (X=F, Cl) [31–33] they are ca. 3.6 Å.

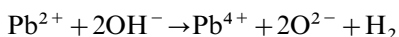
When zeolite A is ion exchanged with aqueous lead nitrate at pH=4.3, a 5% overexchange (6.3  $\text{Pb}^{2+}$  ions per unit cell) occurs [2,4]. With aqueous lead acetate (pH=6.0), a 50% overexchange (9.0  $\text{Pb}^{2+}$  ions per unit cell) occurs [3]. With zeolite X, using a high concentration of lead nitrate, the extent of overexchange is about 23% [5]. In this work, the 18  $\text{Tl}^+$  ions and only 37  $\text{Pb}^{2+}$  ions are needed to balance the total anionic charge, 92–, of zeolite X per unit cell. However a total 49  $\text{Pb}^{n+}$  ions are found. Therefore, 12  $\text{Pb}^{2+}$  ions overexchanged into this structure, which is a 32% overexchange with respect to  $\text{Pb}^{2+}$ .

In this structure,  $\text{Pb}^{4+}$  formed upon evacuation at elevated temperatures by a reaction which may be written (unreduced, with reference to one unit cell) as



The reaction proceeds until all hydrogen atoms and nonframework oxygen atoms have left the zeolite, except for those 17 oxygen atoms per unit cell that can be accommodated by lead ions to form  $\text{Pb}_8\text{O}_4^{n+}$  clusters (Fig. 7). The number of  $\text{Pb}_8\text{O}_4^{n+}$  clusters which can form upon dehydration is limited by the exchangeable cation composition of the zeolite after ion exchange. The fully reduced

net reaction, as previously reported [6], is



Compared with  $\text{Pb}_{64}\text{O}_{32}\text{-X}$  [6], which was prepared using aqueous  $\text{Pb}(\text{O}_2\text{CCH}_3)_2$ , the 32  $\text{Pb}^{2+}$  ions at site I' are still there: they have not been replaced by  $\text{Tl}^+$  ions. The  $\text{Pb}^{n+}$  ions at site II, however, have been partially replaced by  $\text{Tl}^+$  ions. In  $\text{Pb}_{64}\text{O}_{32}\text{-X}$ , only 14 of the 64  $\text{Pb}^{2+}$  ions per unit cell were found to be oxidized to  $\text{Pb}^{4+}$  (about 22%). In this work, only five of the 49  $\text{Pb}^{2+}$  ions are so oxidized (about 10%). Partial  $\text{Tl}^+$  exchange has caused this percentage to decrease.

In summary, site I' is fully occupied by 32  $\text{Pb}^{2+}$  ions. Site II in the supercage is also fully occupied, by 12  $\text{Pb}^{2+}$ , five  $\text{Pb}^{4+}$ , and 15  $\text{Tl}^+$  ions. Site III', the least desirable site, is occupied by three  $\text{Tl}^+$  ions: these are 'excess' with respect to the filled I' and II sites (67–32–32=3). Site I is empty. Five  $\text{Pb}^{2+}$  ions per unit cell have been oxidized to  $\text{Pb}^{4+}$  upon evacuation at elevated temperature, and five molecules of  $\text{H}_2$  have been produced. 12  $\text{Pb}^{2+}$  ions per unit cell have overexchanged into the zeolite. The  $\text{Pb}_4\text{O}_4$  cluster does not appear independently, only as the core of the  $\text{Pb}_4\text{O}_4(\text{Pb}^{n+})_4$  cluster. Only those nonframework oxygen atoms needed to form  $\text{Pb}_4\text{O}_4(\text{Pb}^{n+})_4$  clusters are retained by the zeolite upon dehydration.

#### 4. Supplementary material

Tables of observed and calculated structure factors with esds (six pages) are available for the

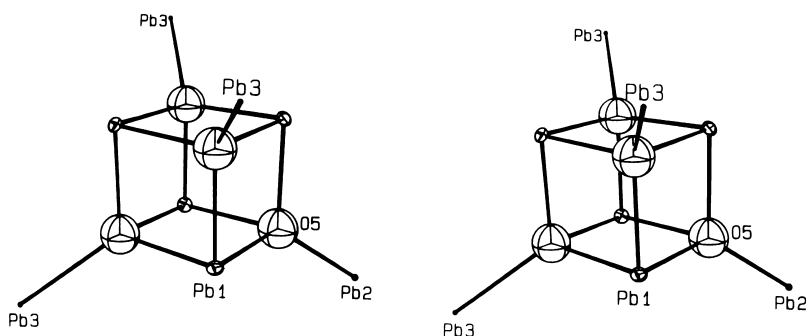


Fig. 7. Stereoview of the  $[(\text{Pb}^{2+})_7(\text{Pb}^{4+})_1(\text{O}^{2-})_4]^{10+}$  cluster within, and extending out of, the sodalite cavity. Ellipsoids of 20% probability are shown.

fully dehydrated structure,  $\text{Pb}_{44}^{2+}\text{Pb}_{5}^{4+}\text{Tl}_{18}^{+}\text{O}_{17}^{2-}-\text{Si}_{100}\text{Al}_{92}\text{O}_{384}$ . Ordering information is given on any current masthead page.

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