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Structural study of Tl-exchanged natural clinoptilolite using Rietveld refinement

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This study presents the exchange of thallium cations in the clinoptilolite channels. Used material is clinoptilolite tuff from Beli Plast deposit, Bulgaria. Fully exchanged thallium forms of HEU–type zeolites have not been reported so far. Here, the ion exchange procedure was performed at 90 °C with 1N solution of $TlNO_3$ for 3 days. The EDS analysis detected major thallium content and small amounts of Ca and Mg. Structural details obtained by PXRD Rietveld refinement reveal thallium positions in the three channels of clinoptilolite microporous structure. Thus, thallium cations are located in three sites: Tl1, (Tl2 and Tl2′ – close to each other), and Tl3 in the channels. Site Tl1 is in the 10-member ring channel A and is occupied by 0.78 Tl cations. This position is shifted towards the centre in comparison with the original sodium position in the channel A. Site Tl2 is in the centre of the 8-member ring channel B, where H_2O molecule usually stays and is occupied by 1.18 Tl cations. A small amount of Tl cations (0.72) are located in site Tl2′ close to Tl2 (distance – 2.42 Å). Site Tl3 with occupation of 2.80 Tl cations is in the 8-member ring channel C near to the original potassium position.

Keywords: clinoptilolite, Tl exchange, Rietveld refinement, EDS.

INTRODUCTION

The mineral group of natural zeolites has a potential for large application and also it is of great interest for crystal-chemical studies related with porous materials [1–3]. The ions exchange is among the important and promising peculiarities of the zeolite porous structure [4]. The spectrum of applications of these minerals covers various branches of industry, ecology, medicine [5–10]. In the exchange process the cations are replaced one another and the incoming ones are integrated and adjusted themselves in various positions into the channel systems. The modified zeolites commonly retain unaffected their microporous structures. The ion-exchanging process in zeolites is typically carried out by replacing Na^+, K^+, and Ca^{2+} with different ions, such as Ag^{2+}, K^+, Cs^+ and Sr^{2+}, etc [11–13]. One of the main methods of purification of toxic and radioactive waste is adsorption deactivation. The most abundant and effective natural zeolite which is used for toxic and radioactive waste-treatment is clinoptilolite. Clinoptilolite has been a focus of researchers for its applications in environmental protection, chemical and other industries because it is stable up to ~650–700 °C and more, and remains unaffected over a wide pH range [14, 15]. Clinoptilolite also has a great potential to keep in its structure toxic and radioactive elements. Different ion-exchanged clinoptilolites are obtained and studied so far [16–23]. Thallium is an extremely toxic metal which contaminates soils and is readily taken up by plants [24]. Fully exchanged thallium forms of HEU–type zeolites have not been reported so far. Detailed description of thallium positions is reported for ZSM5 [25].

The purpose of the present study is to perform structural investigation on the distribution of Tl cations in the structure of ion-exchanged clinoptilolite in order to consider the potential of this zeolite for collector of dangerous polluting cations like Tl^+ and to provide additional crystal-chemical information about the ion-exchange properties of clinoptlolite.

EXPERIMENTAL

The used material is clinoptilolite from Beli Plast deposit, East Rhodopes, Bulgaria.

Ion exchange: 1 g of clinoptilolite, 50 ml 1N $TlNO_3$ solution were placed in a Teflon autoclave

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and heated at 90 °C for 3 days. The autoclave was shaken 5 times daily and the solution of 1N $TlNO_3$ was renewed every day. The Tl-exchanged material was filtered, washed with distilled water (6×200 ml) and dried at room temperature. This Tl-exchanged clinoptilolite was labeled as Tl-cpt.

The chemical composition of natural clinoptilolite was obtained by Inductively Coupled Plasma optical emission spectroscopy (ISP-OES) on a Varian Vista MPX CCD.

The chemical composition of Tl-cpt was determined by EDS microanalysis using a ZEISS SEM LS 25 equipped with an EDAX Trident system. The material under study was preliminary pressed into pellet and then coated with carbon. Series of area EDS analyses were performed in a scanning area regime at acceleration voltage of 15 kV. Sanidine (for Al and Si), diopside (for Ca and Mg), hematite (for Fe) were used as standards. There was a problem to find appropriate standard for thallium. In this study, the pure intensity for TlMa line in the standard file was calculated using linear approximation (R^2=0.99) of the relationship between the pure intensity of Mα line and atomic number of the neighbour to Tl elements in the periodic table - Au, Hg, Pb and Bi. For these calculations, preliminary measurements of intensity of AuMα, HgMα, PbMα and BiMα lines were carried out in metal Au, cinnabar (HgS), galena (PbS) and bismuthinite (Bi_2S_3), respectively.

The obtained analyses were normalized to 100% in view of the uncertainty of water content as determined by the applied method. Then, the obtained compositions were averaged into one average normalized composition which was further used for processing of X-Ray diffraction data and structural refinement of Tl-cpt.

Powder X-ray analyses: Powder X-ray diffraction (PXRD) data were collected at room temperature on a PANalytical X'Pert MPD diffractometer equipped with a Cu X-Ray source (40 kV/40 mA) and an X'Celerator detector. Automatic divergence slits and 0.02 radian soller slits were used. Patterns were collected from 5 to 80° 2θ with a step size of 0.016° 2θ/step at 5 s/step.

The Rietveld method was applied for structural refinement of the sample Tl-cpt. The unit-cell parameters and the atomic coordinates of extra framework cations and H_2O molecules were refined using Bruker AXS Topas v. 4.0 [26] suite of programs. The background was fitted by a Chebyshev polynomial with 20 coefficients and the pseudo-Voigt peak function was applied for peak modelling. The refinement was conducted with the clinoptilolite structural model of ICSD #37061 [27]

RESULTS AND DISCUSSION

The comparison between natural clinoptilolite powder pattern and Tl-cpt (Fig. 1) reveals that the intensity change of the 020 reflection decreased and approached a negligible value. The line 020 is the most influenced one by cation exchange as it was discussed by Petrov 1995 [28]. The lowering of $\{F(020)\}^2$ can be achieved if clinoptilolite under-

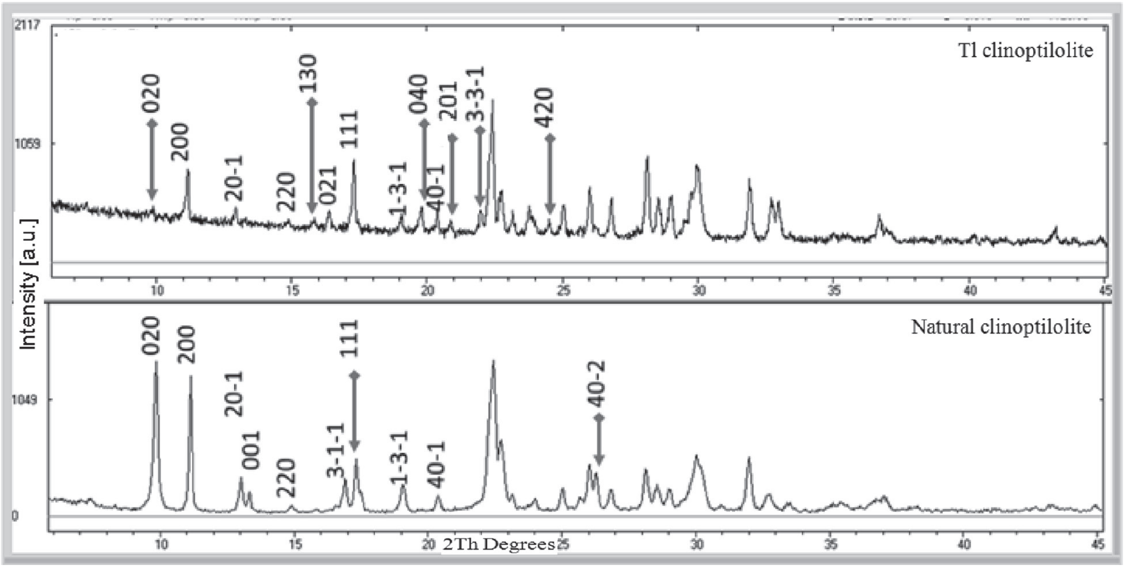

Fig. 1. PXRD patterns of natural (down) and Tl-exchanged clinoptilolite (upper).

goes ion exchange with heavy cations. It was calculated that Tl exhanged cations lower the peak 020 toward zero value of the intensity. Due to the incorporation of Tl cations in the channels other notable differences in intensity of peaks are also observed in the pattern like 001, $3\bar{1}\bar{1}$ and $40\bar{2}$ which decrease (peaks become invisible), while 130, 021, 111, 040, 201, $3\bar{3}\bar{1}$, 420 and others increase their intensity.

The obtained chemical formulae for natural clinoptilolite using ICP OES data is:

$$(Na_{0.23}Ca_{1.83}K_{1.52}Mg_{0.46})Al_{6.31}Fe_{0.07}Si_{29.65}O_{72} \times 20\ H_2O$$

The EDS analysis shows the following composition of the Tl-exchanged clinoptilolite (in wt.%, normalized to 100% without water): SiO_2 – 44.94, Al_2O_3 – 11.64, CaO – 0.90, Tl_2O – 42.00, MgO – 0.20, Fe_2O_3 – 0.32. This composition gives the following crystal chemical formulae of the phase:

$$(Tl_{5.47}Ca_{0.44}Mg_{0.14})Fe_{0.11}Al_{6.32}Si_{29.57}O_{72} \times H_2O.$$

There is a possibility that Mg and Fe are related to mechanical inclusions of other phases. Exclusion of these elements gives the following formulae of the Tl-exchanged clinoptilolite:

$$(Tl_{5.49}Ca_{0.44})Al_{6.34}Si_{29.66}O_{72} \times H_2O.$$

Thus the intensity changes in the PXRD pattern of Tl-cpt and EDS analysis shows that Tl cations almost fully exchange the original cations in clinoptilolite channels.

The structural refinement of clinoptilolite for sample Tl-cpt was performed in several consecutive stages. The first stage of refinement used Tl cations in the extra-framework positions of the model. The framework atomic coordinates were kept fixed. During the next stage of the refinement the extra-framework atomic coordinates were refined and were gradually adjusted to the occupancy obtained from the running refinement and the chemical data. Then, H_2O sites were located and their coordinates and occupancies were also refined. Several times extra-framework and H_2O positions (atomic coordinates) and occupancies were refined and fitted to the experimental data. During the final stage of the refinement isotropic displacement parameters are also refined: first framework positions, then cations and H_2O molecules.

The sites, Wyckoff positions, atomic coordinates, occupancies and isotropic displacement parameters for sample Tl-cpt are listed in Table 1.

The reliability factors and a difference plot showed good agreement between the experimental data and the refined model (Fig. 2, Table 2).

Table 1. Sites, Wyckoff positions, atomic coordinates, occupancies and isotropic displacement parameters Tl exchanged clinoptilolite sample Tlcpt

Site	Wp	x	y	z	Atom	Occ.	Biso.
T1	8j	0.1794	0.1686	0.0978	Si^{4+}	1	1.4(3)
T2	8j	0.2146	0.4108	0.5063	Si^{4+}	1	1.5(3)
T3	8j	0.2083	0.1912	0.7161	Si^{4+}	1	1.3(3)
T4	8j	0.0668	0.2983	0.4176	Si^{4+}	1	1.5(4)
T5	4g	0	0.2173	0	Si^{4+}	1	1.6(3)
O1	4i	0.1981	0.5	0.4565	O^{2-}	1	1.1(3)
O2	8j	0.2330	0.1213	0.6144	O^{2-}	1	1.7(6)
O3	8j	0.1882	0.1535	0.8902	O^{2-}	1	1.8(4)
O4	8j	0.2304	0.1008	0.2473	O^{2-}	1	1.6(4)
O5	4h	0	0.3257	0.5	O^{2-}	1	1.5(3)
O6	8j	0.0805	0.1614	0.0499	O^{2-}	1	1.8(5)
O7	8j	0.1226	0.2296	0.5515	O^{2-}	1	1.8(5)
O8	8j	0.0142	0.2709	0.1891	O^{2-}	1	1.7(6)
O9	8j	0.2153	0.2492	0.1928	O^{2-}	1	1.8(4)
O10	8j	0.1208	0.3708	0.4225	O^{2-}	1	1.8(6)
Tl1	4i	0.548(1)	0	0.182(2)	Tl^{+}	0.194(3)	1.5(6)
Tl2	2d	0	0.5	0.5	Tl^{+}	0.593(4)	1.4(5)
Tl2`	4i	0.515(2)	0	0.190(2)	Tl^{+}	0.180(4)	2.4 (3)
Tl3	4i	0.229(3)	0	0.310(2)	Tl^{+}	0.701(3)	1.1(3)
O12	4i	0.412(2)	0.5	0.287(2)	O^{2-}	1.003(5)	2.6(4)
O13	8j	0.430(3)	0.085(3)	0.106(3)	O^{2-}	0.501(2)	2.2(5)

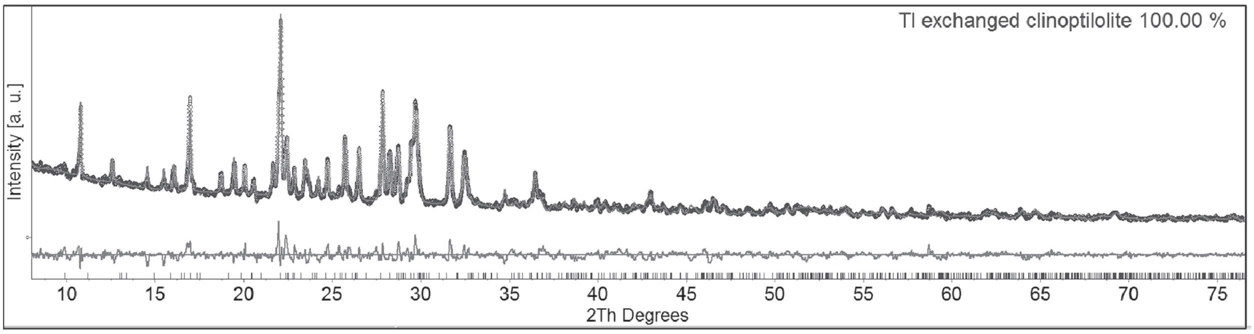

Fig. 2. PXRD difference plot of Tl clinoptilolite.

Structure description and crystal-chemical features of Tl-cpt

Three cationic positions are located in the channels of sample Tl-cpt, namely Tl1, Tl2 (Tl2 and Tl2′ are close to each other) and Tl3 (Fig. 3, Fig. 4). Position Tl1 is in the 10-member ring channel A. This position is shifted toward the centre of the channel in comparison with sodium positions (M1) [29] in the clinoptilolites. The occupation is 0.78 Tl

Table 2. Agreement factors space group and unit cell parameters of Tl-cpt

R_{exp}	6.59	SG	*C2/m*
R_{wp}	7.84	*a*[Å]	17.696(1)
$R_{\text{-p}}$	5.78	*b*[Å]	17.949(1)
R_B	4.01	*c*[Å]	7.412(1)
GOF	1.19	*β*[˚]	116.224(2)
DW	1.12	*V*[Å]	2112.1(2)

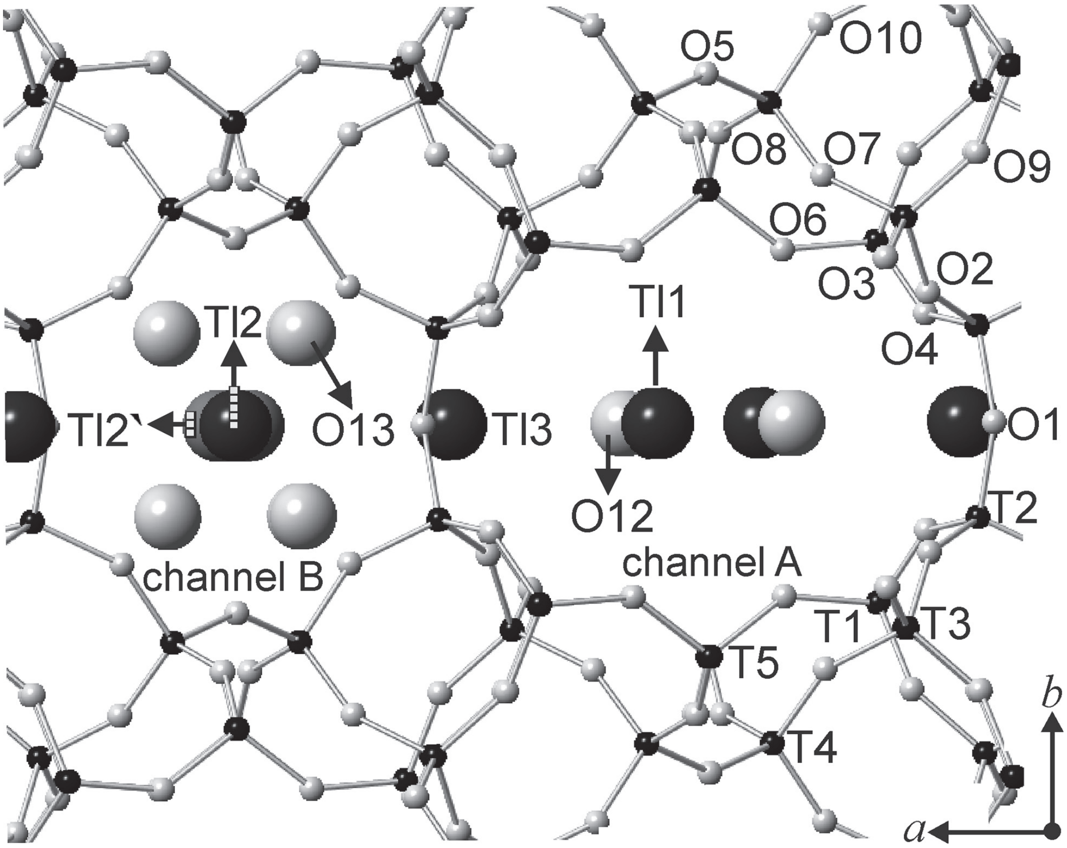

Fig. 3. The tetrahedral framework, positions of cations and H_2O molecules in channel A and B of Tl-exchanged clinoptilolie.

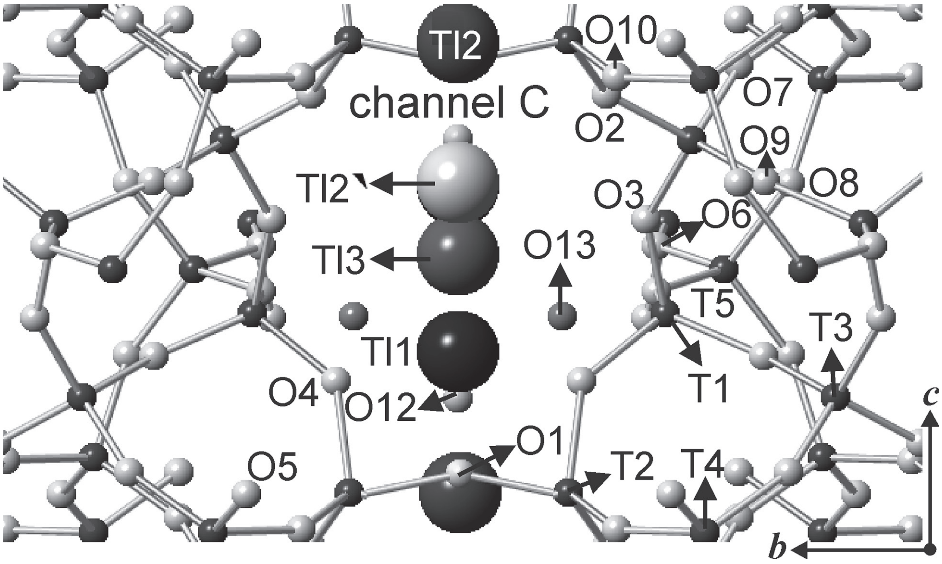

Fig. 4. The tetrahedral framework, positions of cations and H_2O molecules in channel C of Tl-exchanged clinoptilolie.

cations per unit cell. The distances between Tl positions and H_2O molecules as well some of framework oxygen positions are represented in Table 3. The H_2O molecule named O12 (4 molecules per unit cell) coordinate Tl1.

Position Tl2 takes 1.18 Tl^+ per unit cell and locates in the centre of channel B where H_2O molecule usually stays [29]. The H_2O molecules in appropriate distance O13 coordinate position Tl2. Small amounts of Tl^+ 0.72 per unit cell are detected in site Tl2′ close to Tl2 (at a distance of 2.42 Å) and mutual occupation of Tl2 and Tl2′ is forbidden. Position Tl2′ is coordinated by framework oxygens O1 and O10.

Comparison of ion-exchanged zeolites is important both from fundamental point of view sorption (structural modification) and utilization properties (sorption of polluting cations in nature). In the case of Cs exchanged clinoptilolite in channel B, Cs cations are located almost close to the centre [30, 31], or just in the centre [32]. Thallium and cesium are large monovalent cations and they tend to show similarity when occupy the channel B.

Position Tl3 is near to site M3 [29] (channel C) where potassium is usually situated and it is the most occupied by thallium cations (2.1 per unit cell) position. Position Tl3 is coordinated by H_2O molecules in positions O12 and O13 (amounting 4 molecules per unit cel).

The Tl-cpt formula obtained by the refinement is:

$$(Tl_{5.5}Ca_{0.42})Al_{6.35}Si_{29.65}O_{72} \times 8.1\ H_2O$$

Table 3. Selected bond distances between positions of thallium cations, H_2O molecules and framework oxygen

Atom1	Atom2	No	d(Å)	Atom1	Atom2	No	d(Å)
Tl1	Tl1	1x	2.539(24)	Tl2′	O1	1x	2.956(28)
	O12	1x	2.953(43)		O10	2x	2.999(34)
	O6	2x	3.155(23)		O13	2x	3.162(58)
Tl2	Ti2′	2x	2.426(22)	Tl3	O12	1x	2.942(30)
	O13	4x	3.035(38)		O13	2x	2.961(54)
	O5	2x	3.128(31)		O3	2x	3.053(32)
Tl2′	O13	2x	2.042(49)		O4	2x	3.058(29)
	Tl2	1x	2.425(25)	O13	O8	1x	2.906(38)
	Tl2`	1x	2.628(39)		O13	1x	3.062(68)

CONCLUSIONS

Ion exchange of thallium cations in the clinoptilolite channels is studied on clinoptilolite from Beli Plast deposit, Bulgaria. The exchange proceeds almost totally – 5.5 Tl^+ replace about 90% of the original cations in the channels of clinoptilolite. Structural details obtained by PXRD Rietveld refinement reveal thallium positions in the three channels of clinoptilolite microporous structure. Thallium cations are located in three sites: Tl1 (in channel A), Tl2 and Tl2′ in channel B, and Tl3 in channel C. Such structural investigation on the distribution of Tl cations in the structure of ion-exchanged clinoptilolite is important to consider the potential of this zeolite for collector of dangerous polluting cations like Tl^+ and to provide additional crystal-chemical information about the ion-exchange properties of clinoptlolite towards large monovalent cations.

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СТРУКТУРНО ИЗСЛЕДВАНЕ НА Tl-ОБМЕНЕН ПРИРОДЕН КЛИНОПТИЛОЛИТ С ИЗПОЛЗВАНЕ МЕТОДА НА РИТВЕЛД

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(Резюме)

Изследван е обмен на талиеви катиони в каналите на клиноптилолитовата структура. Използваният материал е клиноптилолит от находище „Бели пласт“, България. Данни за напълно обменени на талий форми от HEU–тип зеолити не са съобщавани досега. Йонният обмен е проведен при 90 °C, с използване на 1N разтвор на $TlNO_3$ в продължение на 3 дни. При EDS анализа е установено значително количество талий и малки съдържания на Ca и Mg. Структурните данни са уточнени чрез PXRD по метода на Ритвелд. Анализът показа талиевите позиции в трите типа канали на клиноптилолитовата микропореста структура. Талиевите катиони са разположени в три позиции: Tl1, (Tl2 и Tl2′ близо една до друга) и Tl3. Позиция Tl1 е в канал A, изграден от 10-членни пръстени и е заета от 0.78 Tl катиони. При сравнение с натриевата позиция (канал A) в природните клиноптилолити, Tl1 се измества в посока към центъра на канала. Позиция Tl2 е в центъра на канал B, изграден от 8-чleненни пръстени, където обикновено застава водна молекула, и е заета от 1.18 Tl катиони. Малко количество от Tl катиони (0.72) се намира в положение Tl2′, близо до позиция Tl2 (разстояние – 2.42 Å). Позиция Tl3 е със заетост 2.80 Tl катиони. Тя е в канал C, изграден от 8-члененни пръстени и се намира близо до калиевата позиция при природните клиноптилолити.