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THEORETICAL
INORGANIC CHEMISTRY

Modeling of Self-Organization Processes in Crystal-Forming Systems: Templated Precursor Nanoclusters T48 and the Self-Assembly of Crystal Structures of 15-Crown-5, Na-FAU, 18-Crown-6, Na-EMT, and Ca,Ba-TSC Zeolites

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Abstract—The combinatorial and topological modeling of packings of symmetry-related nanoclusters T48 (diameter: ~16 Å, symmetry $\bar{4}3m$) is performed. The packings are 1D claims S_3^1 and 2D microlayers S_3^2, which give rise to 3D structures S_3^3. For three of the five framework structures, correspondence was established with zeolite FAU (Faujasite, *Fd*-3*m*, $Z = 4$ T48), EMT ($P6_3/mmc$, $Z = 2$ T48), and TSC (Tschortnerite $Fm\bar{3}m$, $Z = 8$ T48). Combinatorial topological analysis methods (the ToposPro program package) were used to model the steps of zeolite crystal structure self-assembly. The underlying idea of these methods consists in that the basal 3D network of the zeolite structure is designed as a graph, where the nodes correspond to the centroid positions of clusters T48. For FAU, the basal 3D network corresponds to the copper cubic strucutre (CN = 12); for EMT, it corresponds to the hexagonal (H) strucutre of magnesium (CN = 12); and for TSC, to the cubic structure of polonium (CN = 6). The symmetry and topology code of zeolite strucutre formation has been restored in the form of the sequence of significant elementary events that characterize the shortest (rapidest) program of convergent cluster self-assembly. The functional role played by 15-crown-5 and 18-crown-6 template molecules has been established to consist in the stabilization of the primary chains and microlayers of FAU and EMT frameworks and the relevant network of diamond and graphite topological types. The model for 3D structure self-assembly from clusters T48 is capable of explaining the morphogenesis of single crystals to form regular octahedra in FAU, hexagonal prisms in EMT, and regular cubes in TSC.

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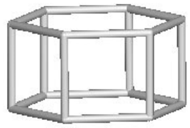
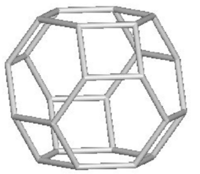
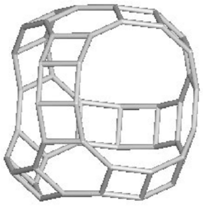
Supramolecular chemistry is concerned with problems of multistage modeling of crystal structures, that is, crystal engineering “from a molecule (cluster) to a crystal” [1–10]. The scenario of local binding of clusters at the stage of supracluster formation and during crystal structure self-assembly is under study. The ability of a cluster to form more than one crystal structure is taken into account. Variant structures of known crystal structures are considered, and new hypothetical crystal structures are modeled [3–6].

The problem of combinatorial topological modeling of one-, two-, and three-dimensional packings with the set type of polyhedral cluster is tightly related to the modeling of self-assembly of zeolite framework structures involving the consecutive steps of 1D primary chain → 2D microlayer → 3D microframework. There are known 225 topologically different types of 3D zeolite frameworks [11]. The topological model of 3D zeolite frameworks consists of 3-periodical, 4-coordinated 3D T-networks [11–15]. 3D zeolite networks can topologically be defined by the listing of complementary polyhedral tiles T_n, where n is the number of tetrahedral T-nodes. Tiles T_n characterize all polyhedral cavities of zeolites and form the normal (face-to-face) division of the crystal space [12]. The 3D topological type of zeolite framework is determined by the set of 3D tiles.

The greatest tiles in zeolites are t-fau, t-wou, and t-vsr tiles; the corresponding polyhedra have 48 T-nodes in the FAU framework, 60 T-nodes in the EMT framework, and 90 T-nodes in the TSC framework (Fig. 1). These large tiles characterize the uniqueness of the structure types of those zeolites. Presumably, the self-assembly of frameworks with large tiles involves large 3D precursor nanoclusters.

The polyhedral 3D cluster T12 (the t-hpr tile shaped as a hexagonal prism) is most frequently recognized in 3DT zeolite frameworks as shown by statistical data [12, 13] (Fig. 1). In some zeolite crystal structures including such as FAU, EMT, and TSC, cluster

(a)

Tile			
(V, E, F) Symmetry Position Tile type	(12, 18, 8) $\bar{3}m$ 16*c* t-hpr	(24, 36, 14) $\bar{4}3m$ 8*a* t-toc	(48, 72, 26) $\bar{4}3m$ 8*b* t-fau

(b)

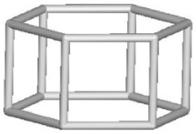
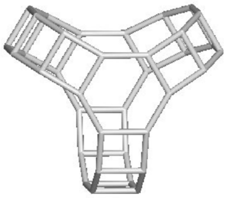
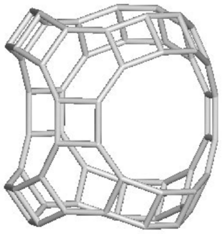
Tile				
(V, E, F) Symmetry Position Tile type	(12, 18, 8) 6*m*2, 2/*m* 2*c*, 6*g* t-hpr	(24, 36, 14) 3*m* 4*f* t-toc	(36, 54, 20) 6*m*2 2*d* t-wof	(60, 90, 32) 6*m*2 2*b* t-wou

Fig. 1. Tiles in tetrahedral zeolite frameworks: (a) FAU, (b) EMT, and (c) TSC. The values of V, E, and F in parentheses are equal to the numbers of vertices, edges, and faces in the tile.

T12 contains all crystallographically unique T-nodes of the framework and is the only assembly structural unit whose packing fully determines the topology of the whole 3D network of the zeolite [12–15]. Earlier [16] by means of computer methods (TOPOS program package [17]), we determined the precursor nanocluster T48 for TSC (Tschoertnerite, a = 31.62 Å, V = 31.614 Å^3, space group $Fm\bar{3}m$ [18]); that precursor nanocluster had hierarchic structure in the form of four connected clusters T12, which corresponded to tile t-hpr. The precursor nanocluster T48 has the physical meaning of a cluster that forms a 1D primary chain of the crystal structure and determines the values of unit cell parameters [7–10]. A TSC unit cell contains eight clusters T48 with symmetry $\bar{4}3m$. The size of precursor cluster T48 in TSC is $a/2$ = 31.62 Å/2 = 15.81 Å.

This study aims at the combinatorial topological modeling of one-, two-, and three-dimensional packings of symmetry-related suprapolyhedral clusters T48. These packings are symmetrically and topologically feasible 1D chains S_3^1 and 2D microlayers S_3^2, which can form series of polytypic 3D zeolite structures. The theoretically derived models of five structures S_3^3 are compared to 225 known types of zeolite frameworks, and for three of them, correspondence is found with FAU [11, 19] (the mineral Faujasite, $Fd\bar{3}m$, Z = 4 T48), EMT [11, 19, 20] (a synthetic phase, $P6_3/mmc$, Z = 2 T48), and TSC (Tschoertnerite). The symmetry and topology code of zeolite strucutre formation has been restored in the form of the sequence of significant elementary events that characterize the shortest (rapidest) program of convergent cluster self-assembly. The functional role played by 15-crown-5 (15C5) and 18-crown-6 (18C6) template molecules in the stabilization of the primary chains and formation of microlayers of the FAU and EMT frameworks is considered.

(c)

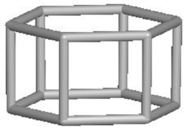
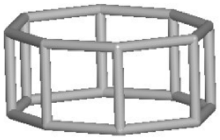
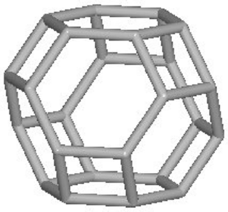
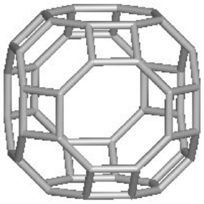
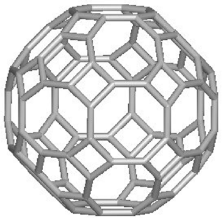
Tile			
(V, E, F) Symmetry Position Tile type	(12, 18, 8) $.3m$ $32f$ t-hpr	(16, 24, 10) $m.mm$ $24d$ t-opr	(24, 36, 14) $\bar{4}3m$ $8c$ t-toc
Tile			
(V, E, F) Symmetry Position Tile type	(48, 72, 26) $m3m$ $4a$ t-grc	(96, 144, 50) $m3m$ $4b$ t-vsr	

Fig. 1. Contd.

COMBINATORIAL TOPOLOGICAL MODELING OF CLUSTER T48 PACKINGS

Let us consider the combinatorial topological properties of cluster T48, which is formed of four hexagonal prisms T12. Cluster T48 has high point symmetry $g = \bar{4}3m$, and $3m$ (Fig. 2). The crystal structures obtained by self-assembly from clusters T48, will be described by high-symmetry space groups, namely cubic space groups which have elements with point symmetry $g = \bar{4}3m$, and hexagonal space groups with $g = 3m$.

Any supracluster built of clusters $(\mathrm{T48})_n$ will represent packings; that is, clusters T48 have no common T-nodes at all self-assembly steps.

Cluster T48 has 24 vacant vertices (Fig. 2). There are three possible variant distributions of all vacant nodes used in the self-assembly of a 1D primary chain, a 2D microlayer, and 3D microframework.

First Variant Distribution of Nodes 4T + 4T + 16T

The self-assembly of primary chain CH-1 from clusters T48 related by symmetry plane $g = m$, in the direction of X_1 and $-X_1$ involves 2 + 2 = 4 cluster nodes (Fig. 3). The stabilization of clusters in the chain will be most efficiently provided by location of template molecules in between clusters in the symmetry plane $g = m$.

The self-assembly of microlayer LR-1 from parallel lying chains CH-1 related by symmetry plane $g = m$ in the direction X_2 and $-X_2$ involves 2 + 2 = 4 cluster nodes (Fig. 4). The stabilization of clusters in the chain will be most efficiently provided by location of template molecules in between clusters from neighboring chains. In addition, template molecules can be located in the center among four clusters T48.

Framework FR-1. The self-assembly of the framework from microlayers LR-1 in the direction X_3 and $-X_3$ involves all the 8 + 8 = 16 cluster nodes. This variant involves the superposition of microlayers with displacement; all eight vertices of cluster T48 will be complementarily connected to the vertices of four clusters T48 from the neighboring layer.

Framework FR-2. The connection of microlayers LR-1 in the direction X_3 and $-X_3$ through symmetry plane $g = m$ (without displacement) involves four

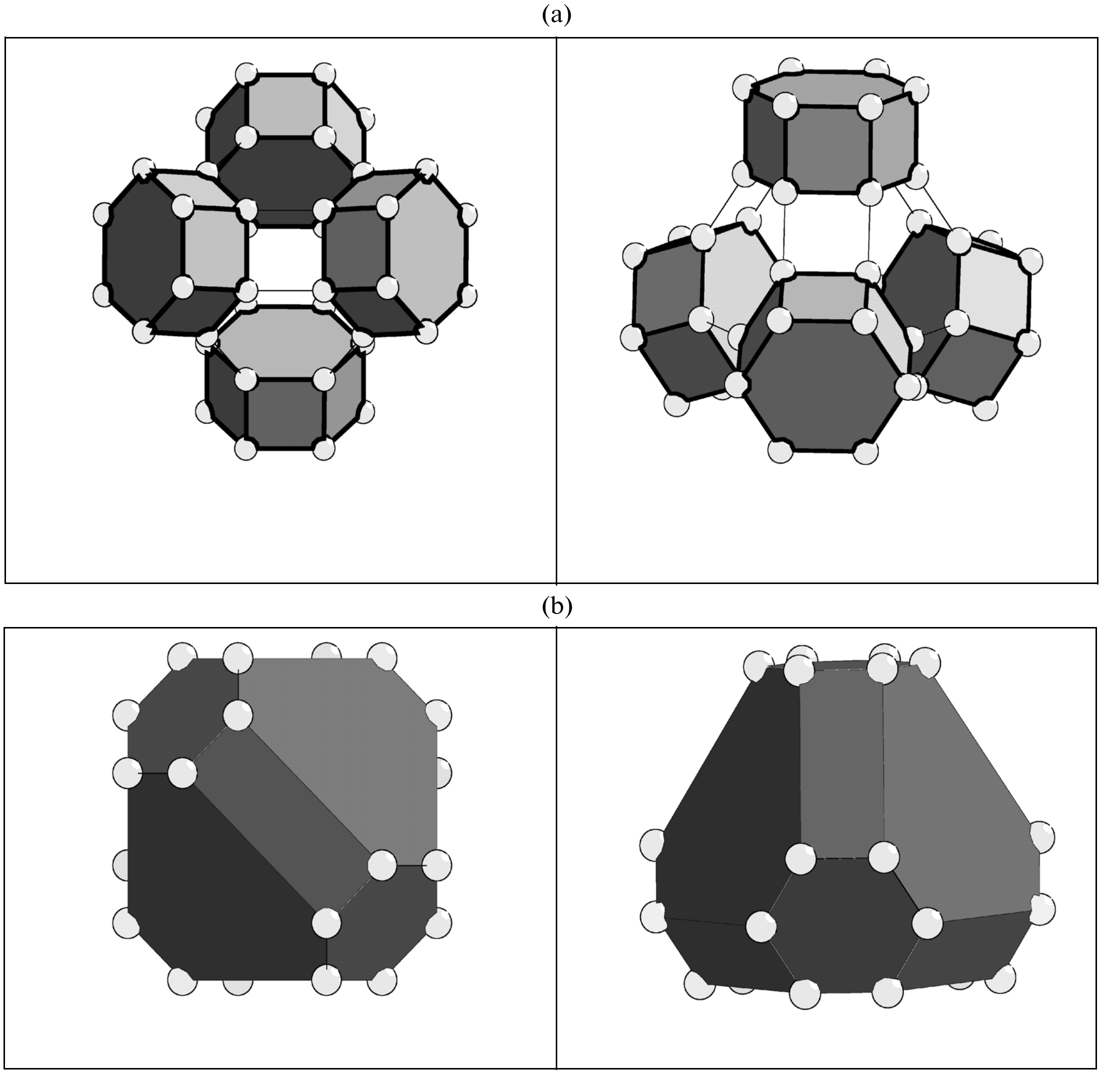


Fig. 2. Cluster T48 of four complementarily connected prisms represented as (a) four hexagonal prisms T12 and (b) a polyhedron of 24 vertices which are involved in polymerization.

upper vertices of cluster T48; four (neighboring) vertices remain vacant.

Second Variant Distribution of Nodes 4T + 8T + 12T

The self-assembly of primary chain CH-1 from clusters T48, related by symmetry plane $g = m$, in the direction X_1 and $-X_1$ involves 2 + 2 = 4 cluster nodes (Fig. 4). The stabilization of clusters in the chain will be most efficiently provided by location of template molecules in between clusters T48 in symmetry plane m.

The self-assembly of microlayer LR-2 from chains CH-1 arranged with displacement in the direction X_2 and $-X_2$, involves 4 + 4 = 8 cluster nodes (Fig. 5). An additional stabilization of the microlayer can be provided by locating template molecules in between three clusters T48 in a small cavity.

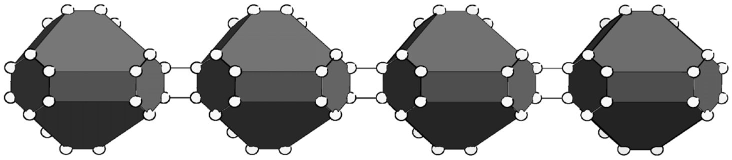
Framework FR-3. The self-assembly of the framework involving 6 + 6 cluster nodes involves the superposition of layers with displacement; all six vertices of cluster T48 will be connected to the free vertices of three clusters T48 from the neighboring layer.

Framework FR-4. The connection of microlayers LR-2 in the direction X_3 and $-X_3$ through symmetry plane $g = m$ (without displacement) involves six vertices of each cluster T48 and six vertices of cluster T48 from the neighboring layer.

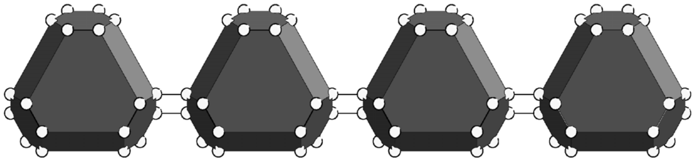
Third Variant Distribution of Nodes 8T + 8T + 8T

The self-assembly of primary chain CH-2 from clusters T48, related by symmetry plane $g = m$, in the direction X_1 and $-X_1$ involves 4 + 4 = 8 cluster nodes (Fig. 4). Primary chain CH-2 has no positions where large template molecules would be located in between clusters.

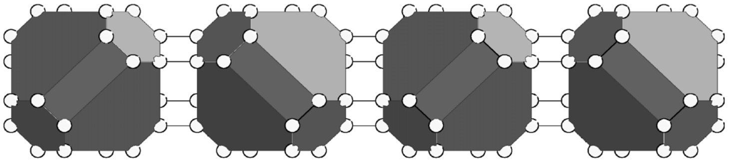
The self-assembly of microlayer LR-3 from chains CH-2, related by symmetry plane $g = m$, in the direc-



Chain CH-1, $P_{\text{loc}} = 2$



Chain CH-1, $P_{\text{loc}} = 2$



Chain CH-2, $P_{\text{loc}} = 4$

Fig. 3. Chains CH-N built of clusters T48 related by symmetry plane *m*.

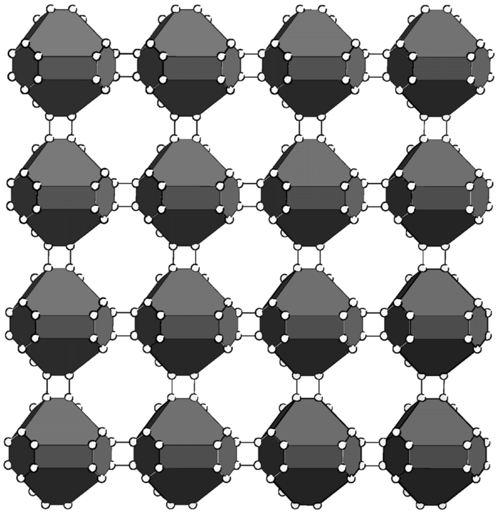
tion X_2 and $-X_2$ involves $4 + 4 = 8$ cluster nodes. Template molecules can be located in between four clusters T48. There is an alternation of two cavities having considerably differing sizes in a 2D layer.

Framework FR-5. When microlayers LR-3 are connected in the direction X_3 and $-X_3$ through symmetry plane $g = m$ (without displacement), four vertices of each cluster T48 will be connected to four vertices of each cluster T48 from the neighboring layer.

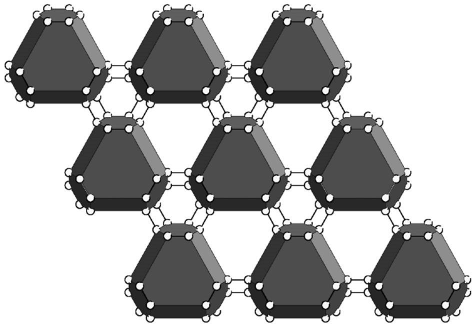
METHODS USED IN COMPUTER ANALYSIS

Computer methods (ToposPro program package [17], the database comprising 225 types of zeolite frameworks) served us to establish the correspondence if the derived structures with known zeolites. The search for structures involves setting a local structural fragment represented as a graph.

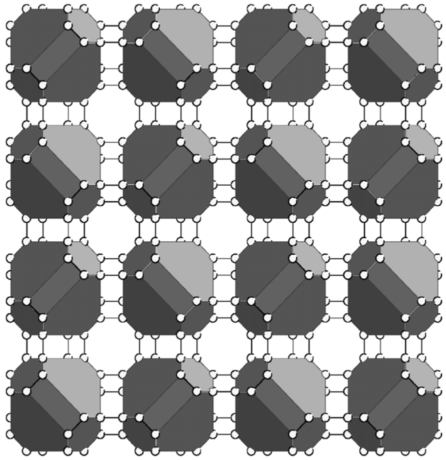
The algorithm of geometrical and topological analysis using the ToposPro program package comprised the steps of:



Microlayer LR-1



Microlayer LR-2



Microlayer LR-3

Fig. 4. Microlayers LR-N obtained by self-assembly from primary chains CH-N.

—representing the zeolite crystal structure as graph *G*1, which corresponds to the entire bond system of T-atoms;

—searching for local structural fragments in the form of clusters T48 in graphs *G*1;

—representing the zeolite crystal structure as graph *G*2, which characterizes the basal network type where the graph vertices correspond to the centroids of clusters T48 and the edges correspond to connections between them; and

—determining the topology of graphs *G*1 and *G*2 using IsoTest software.

The topological types of frameworks FR-1, FR-3, and FR-5 obtained in this manner corresponded to the framework zeolite structures of FAU (Faujasite, $Z = 4$ T48, $Fd\bar{3}m$), EMT ($Z = 2$ T48, $P6_3/mmc$), and TSC (Tschoertnerite, $Z = 8$ T48, $Fd\bar{3}m$).

The clusters T12 recognized in zeolites FAU, EMT, and TSC, which form supraclusters T48, are shown in Fig. 5. The positions in the center of cluster T12 in between six-membered rings are fully filled, and/or there is random occupation of the central position or above and below the six-membered rings.

SELF-ASSEMBLY OF CRYSTAL STRUCTURES

Interparticle interactions in a crystal-forming system have a certain spatial and temporal sequence of elementary events [7–10]. This sequence can be written as the program of structure self-assembly from nanoclusters S_3^0 (as some final sequence of events).

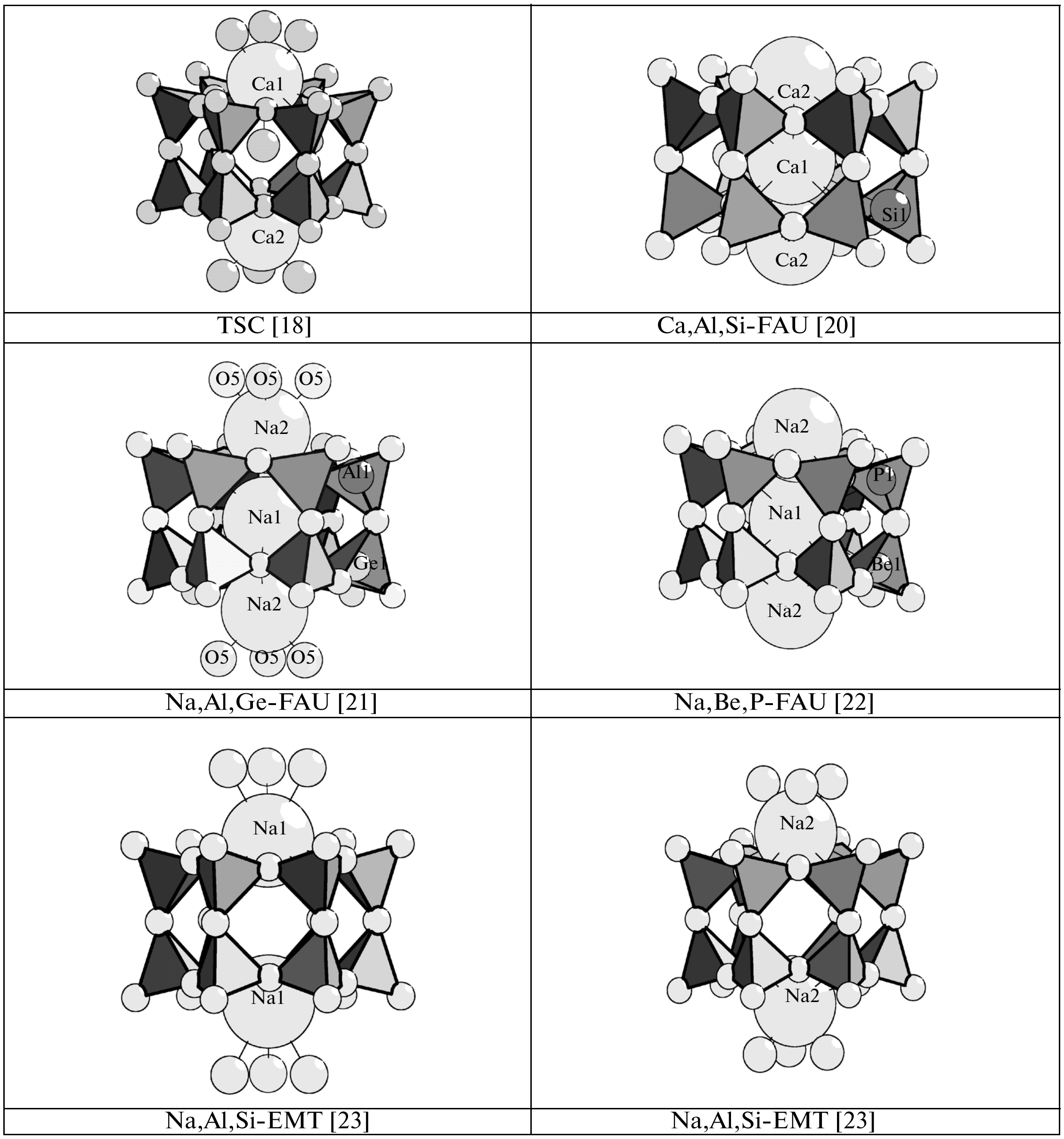
The modeling of macrostructure involves the determination of the hierarchic sequence of its self-assembly in the crystallographic space *XYZ*; that is, the symmetry and topology code of macrostructure formation is restored as the sequence of significant elementary events which characterize the shortest (rapidest) program of convergent cluster self-assembly.

The minimal number of zero-level precursor clusters S_3^0, that form a third-level precursor nanocluster (microframework S_3^3) is eight. This number follows from the fact that each translation vector should be defined by a pair of orientation relations of precursor clusters S_3^0 in the three-dimensional space (X_1, X_2, X_3).

Structural models of micromatrices (structural blocks) of eight complementarily connected clusters T48 2 × 2 × 2 in size are considered below.

Zeolite FAU Structure Type

The derived type of framework FR-1 corresponds to the mineral Faujasite whose compositions is $(Ca^{2+},Na_2^+)_{29}(H_2O)_{240}Al_{58}Si_{134}O_{384}$ [11]. In synthetic Na-FAU aluminosilicates, the Si/Al variation range is bounded to 1.5–3 [19]. An Na-FAU aluminosilicate having a greater proportion Si/Al = 4–5 can be prepared only using 15C5 template molecules [19] (Fig. 6). Crystal structures are known for the following synthetic



TSC [18]

Ca,Al,Si-FAU [20]

Na,Al,Ge-FAU [21]

Na,Be,P-FAU [22]

Na,Al,Si-EMT [23]

Na,Al,Si-EMT [23]

Fig. 5. Templated clusters T12 in zeolite structures.

compounds: Ca,Al,Si-FAU [20], Na,Al,Ge-FAU [21], and Na,Be,P-FAU [22].

Crystallographic data. The cubic unit cell parameters for Ca,Al,Si-FAU [20]: a = 24.9686 Å, V = 15566.20 Å^3, space group $Fd\bar{3}m$ (No. 227), Z = 192 T (4 × 48 T = 192). A dehydrated single crystal shaped as octahedron 0.16 mm in size has been studied.

The cubic unit cell parameters for 15C5,Na-FAU [19]: a = 24.56 Å, V = 14814.4 Å^3, space group $Fd\bar{3}m$ (No. 227), Z = 192 T (4 × 48 T = 192). The crystal structure has not been solved. Single crystals have been obtained as an octahedron 3 μm in size. As probed by chemical analysis, there are eight 15C5 template molecules in the unit cell per 192 T-tetrahedra [19], or two 15C5 molecules per cluster T48.

The set of elements with the point symmetry for space group $Fd\bar{3}m$ (No. 227, the group order: 192) comprises: $\bar{4}3m$ (positions 8a and 8b), $\bar{3}m$ (positions 16c and 16d), 3m (positions 32e), 2mm (positions 48f), and other.

The set of tiles: t-hpr-12T, t-toc-24T, and t-fau-48T (Fig. 1).

A 15C5 template molecule centered by an Na atom can be located only in cavity t-fau (in the center or slightly eccentrically). The multiplicity of positions 8b corresponds to eight molecules in a unit cell, which matches chemical analysis data [19]. Further, we will

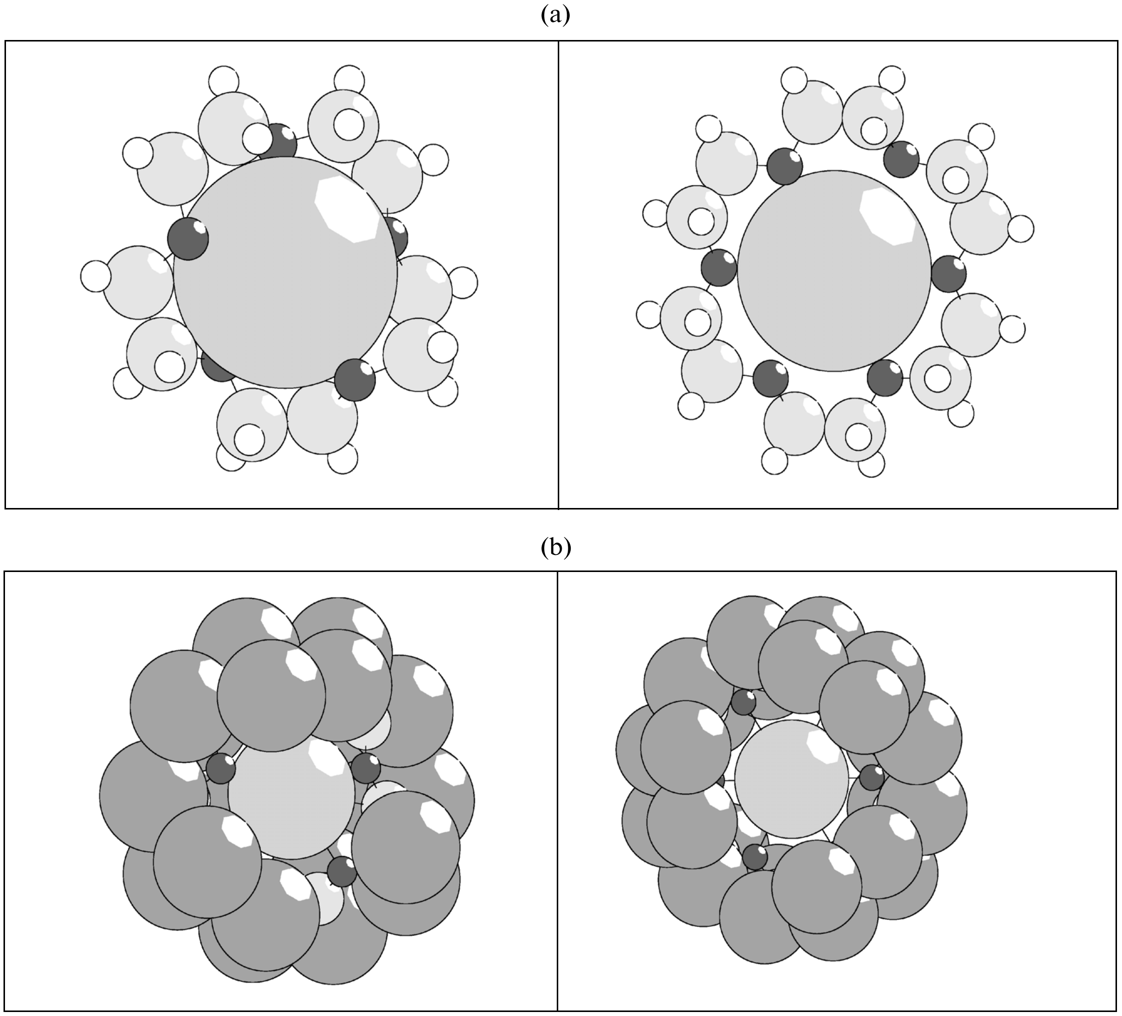


Fig. 6. Structural models of a 15C5 molecule (left) and a 18C6 molecule (right) with a Na atom in the center represented as (a) covalently bonded atoms and (b) with indication of boundaries of the region of hydrogen atoms that perform noncovalent binding with cage O atoms.

consider the structural model of a framework compound with 15C5 molecules positioned in the center of cavity t-fau.

Precursor cluster. Precursor supracluster T48 in the crystal structure retains the high symmetry $\bar{4}3m$. The topology of the internal cavity of the supracluster corresponds to tile t-toc-24T. Sodium atoms reside inside this cavity in six-membered rings between T12.

The topological type of a basal 3D network for precursor clusters T48 corresponds to the copper cubic structure with CN = 12 (Fig. 7).

Primary chain. The self-assembly of primary chains CH-1 (Fig. 8) by the identity mechanism of pair interactions (Fig. 3) with the connectivity index $P_{\mathrm{loc}} = 2$ occurs in the direction of a diagonal in plane *XY* (Fig. 2). The symmetry of the dimer is $g = 2mm$ (position 48*f*).

The center-to-center distance between supraclusters corresponds to one half the diagonal of the cubic cell (d = 17.37 Å) and exactly determines the value of the cubic unit cell parameter according to $d^2 = 2a^2$; that is, a_{cub} = 24.56 Å.

A 15C5 template molecule is located between two clusters T48 and occupies position 8*b*, which corresponds to the center of the cavity (to tile t-fau). The H atoms of the 15C5 template molecule are bonded to O atoms. Thereby, the mutual arrangement of two connected clusters T48 is fixed in the space.

Microlayer. Microlayer LR-1 is formed through connection of two parallel arranged short chains CH-1 of plane *XY* (Figs. 4, 9). In a microlayer, neighboring clusters T48 from different primary chains are connected by the identity scenario of pair interactions with the connectivity index $P_{\mathrm{loc}} = 2$.

The center-to-center distance between supraclusters from different chains corresponds to one half the diagonal of the cubic cell (17.37 Å).

Upon microlayer assembly, 15C5 molecules are arranged between neighboring clusters T48 from dif-

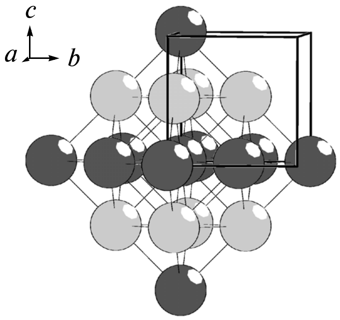
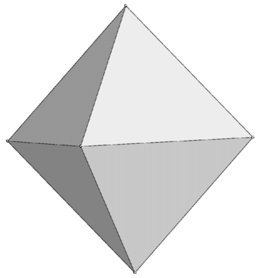
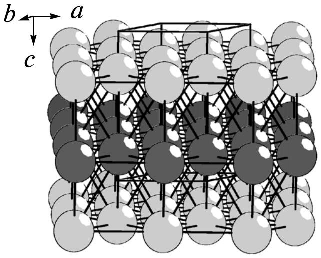
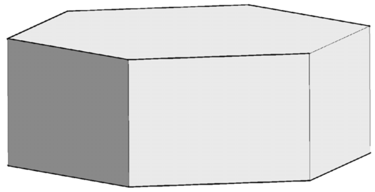
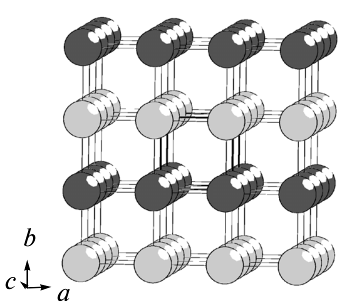
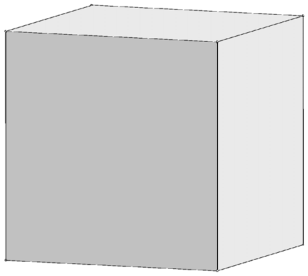
	
Basal network Cu, CN = 12	Monocrystal 15C5,Na-FAU
	
Basal network Mg, CN = 12	Monocrystal 18C6,Na-EMT
	
Basal network Po, CN = 6	Monocrystal TSC and CHA

Fig. 7. Basal networks and single-crystal forms for zeolites FAU, EMT, and TSC.

ferent primary chains and in the center of the supracluster. Noteworthy, the position of the center of the 15C5 molecule in the center of the supracluster also corresponds to 8*b*, that is, to the center of tile t-fau. The H molecules of the 15C5 template molecule are bonded to O atoms. Thereby, the mutual arrangement of four connected clusters T48 is fixed in the space.

Microframework. Microframework S_3^3 is formed upon packing of templated microlayers with displacement (Fig. 10). The supracluster center occupies position 48*f* with symmetry 2*mm*. The size of 2 × 2 × 2 structural block built of eight complementarily connected clusters T48 in the direction of axis *Z* corresponds to $a = 24.968$ Å, and this value will correspond to the minimal value of the crystal growth step.

The multiple 3D condensation of 2 × 2 × 2 structural blocks, which are complementarily connected at their boundaries, leads to the self-assembly of 3D macrostructure.

The arrangement of centers of 15C5 template molecules in the 3D framework corresponds to the diamond 3D network (Fig. 10).

The cluster self-assembly model of the 3D structure from supraclusters T48 is capable of explaining the morphogenesis of FAU single crystals with the formaiton of regular octahedra (Fig. 7).

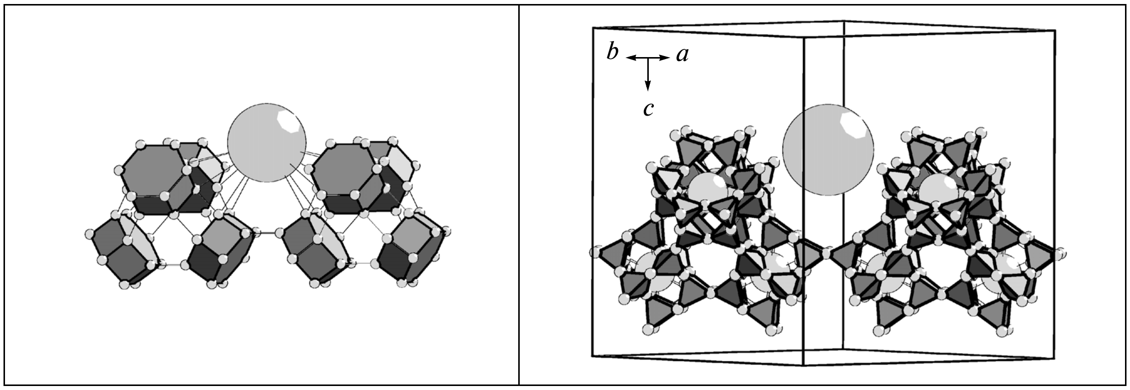


Fig. 8. 15C5,Na-FAU. A primary chain of two supraclusters T48. Left-hand panel: supraclusters imaged as graphs. Right-hand panel: the same as suprapolyhedral clusters.

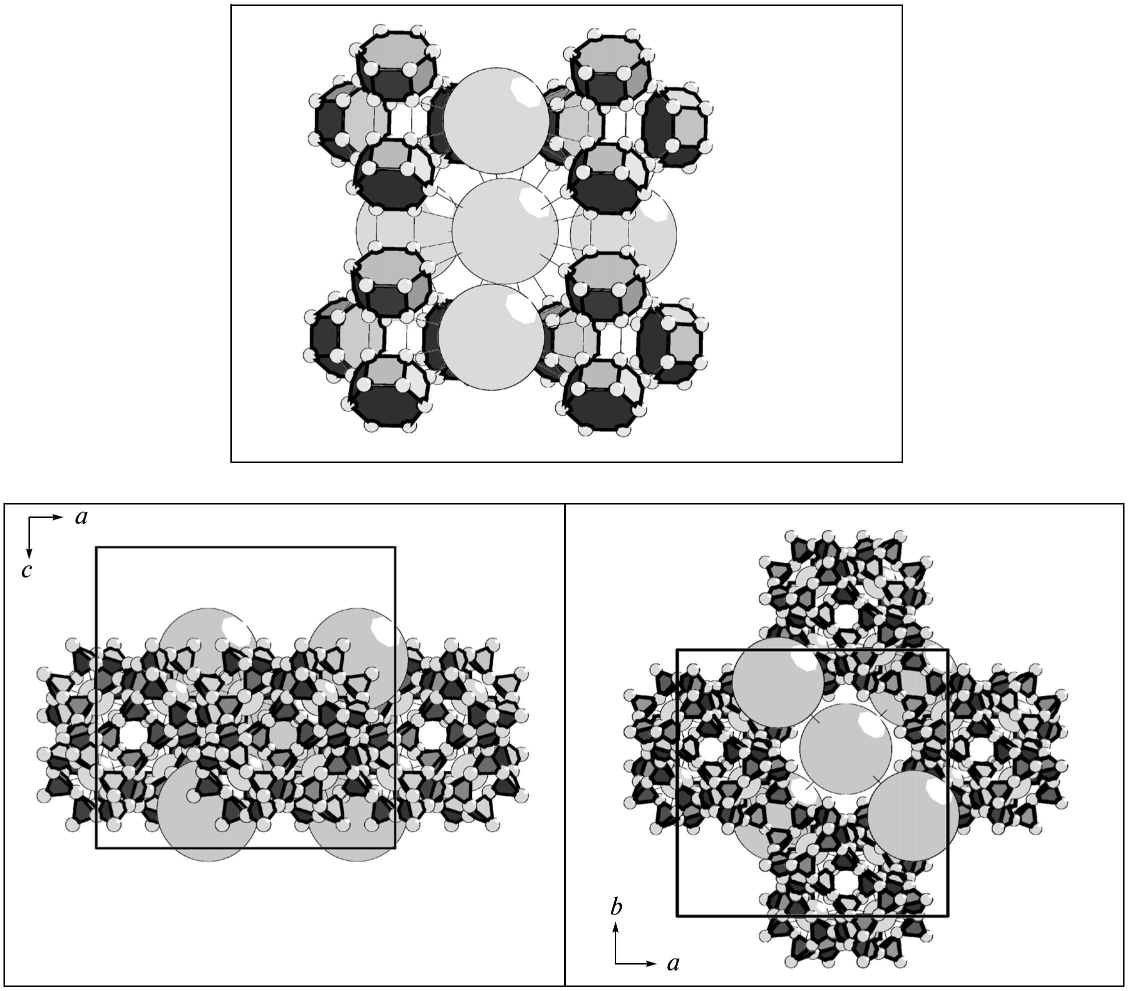


Fig. 9. 15C5,Na-FAU. A microlayer of two primary chains. Upper panel: supraclusters imaged as graphs. Lower panel: the same as suprapolyhedral clusters (two projections).

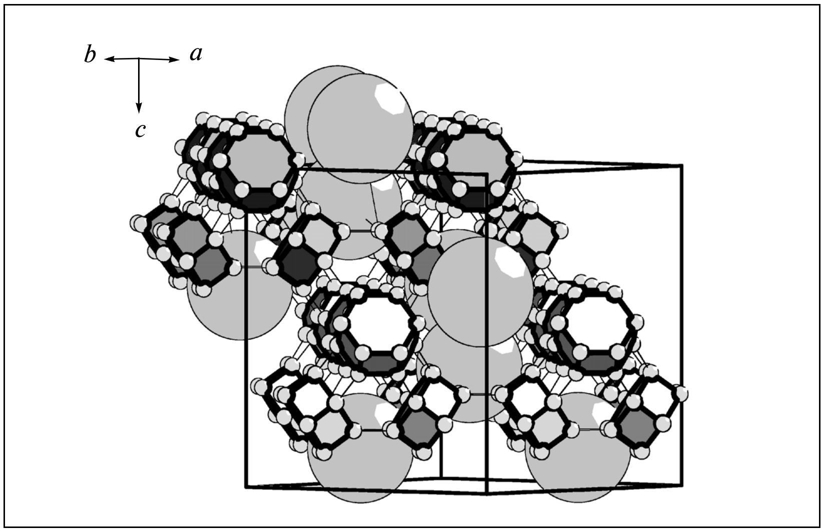


Fig. 10. 15C5,Na-FAU. A microframework of two microlayers. Supraclusters imaged as graphs.

EMT Zeolite Structure Type

Single crystals of aluminosilicate 18C6,Na-EMT as flattened hexagonal prisms 3 μm in size were first obtained with the use of 18C6 template molecule (Fig. 6) under the same conditions as used to prepare 15C5,Na-FAU [19]. When other organic molecules were used, hydrogel was obtained [19].

Crystallographic data. The hexagonal unit cell parameters for 18C6,Na-EMT [19]: $a = b = 17.35$ Å, $c = 28.29$ Å, $V = 7375$ Å^3. Chemical analysis shows that there are four 18C6 template molecules in the unit cell per 96 T-tetrahedra [19] or two 18C6 template molecule per cluster T48.

The 18C6,Na-EMT crystal structure was determined X-ray powder diffraction (random and ordered site occupation by Na and C atoms; H atoms were not located) [23]. The hexagonal unit cell parameters for EMT [23]: $a = b = 17.37$ Å, $c = 28.36$ Å, $V = 7414.9$ Å^3, space group $P6_3/mmc$ (No. 194), hP494. In the unit cell, there are four 18C6 template molecules per 96 T-tetrahedra. Two crystallographically unique 18C6 template molecules centered by N atoms were found.

The set of elements with the point symmetry for space group $P6_3/mmc$ (No. 194, group order: 96): $\bar{3}m$ (positions 2a), $\bar{6}m2$ (positions 2b, 2c, 2d), $3m$ (positions 4e, 4f), $2/m$ (positions 6g), $mm2$ (6h), and other.

The set of tiles: t-hpr-12T, t-toc-24T, t-wof-36T, and t-wou-60T (Fig. 1).

The first crystallographically unique 18C6 template molecule randomly (with 50% probability) occupies position 4 in the tile t-wou-60T (Fig. 1); the displacement from the center of the cavity is 3.37 Å (the coordinates of the center of the molecule are 0, 0, 0.369).

The second crystallographically unique 18C6 molecule occupies the special position (1/3, 2/3, 1/4) (symmetry $\bar{6}m2$, position 2c) in an ordered manner.

Precursor cluster. Supracluster T48 retains point symmetry $3m$ in the crystal structure; clusters T12 have different symmetries (Fig. 1).

The topological type of the basal 3D network for precursor clusters T48 corresponds to the magnesium hexagonal structure with CN = 12 (Fig. 7).

Primary chain. The self-assembly of primary chains CH-1 follows the identity mechanism of pair interactions (Fig. 3) in the direction of axis X (Fig. 11). The symmetry of supracluster S_3^1 corresponds to $g = m$ (the center in positions 12k). The center-to-center distances between supraclusters determine the value of the translation vector $a_{\text{hex}} = 17.35$ Å. Accordingly, the supracluster has the size of 17.35 Å.

The 18C6 template molecule is located in plane $g = m$ between two clusters T48. The H atoms of the 18C6 template molecule are bonded to O atoms. The mutual arrangement of two connected clusters T48 is thereby fixed in the space.

Microlayer. Microlayer LR-2 is formed through connection, in plane XY, of parallel lying short chains (Fig. 12). In the microlayer, neighboring clusters T48 from different primary chains are connected by the identity mechanism of pair interactions (Fig. 4). New 18C6 molecules are arranged between three clusters T48.

Microframework. Microframework S_3^3 is formed through packing of templated microlayers, which are related by a gliding plane, in the direction of axis c (Fig. 13). When structural blocks of eight complementarily connected clusters T48 of size 2 × 2 × 2) are packed, the distance between them ($c = 28.29$ Å) will

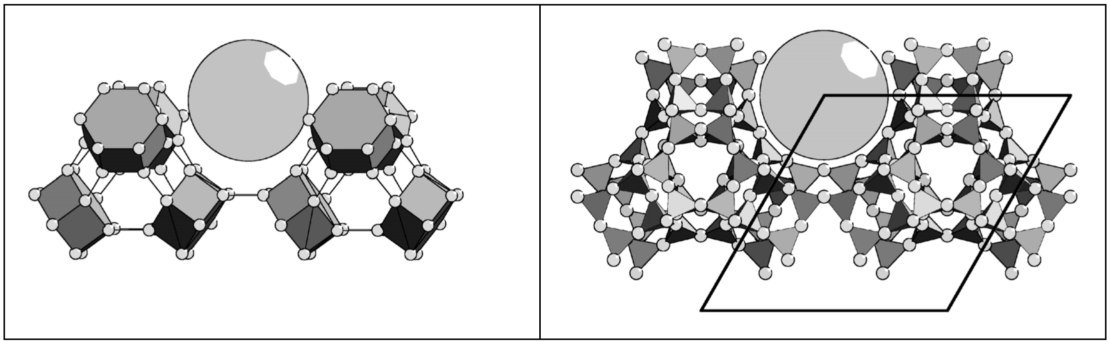


Fig. 11. 18C6,Na-EMT. A primary chain of two supraclusters T48 (two projections). Left-hand panel: supraclusters imaged as graphs. Right-hand panel: the same as suprapolyhedral clusters.

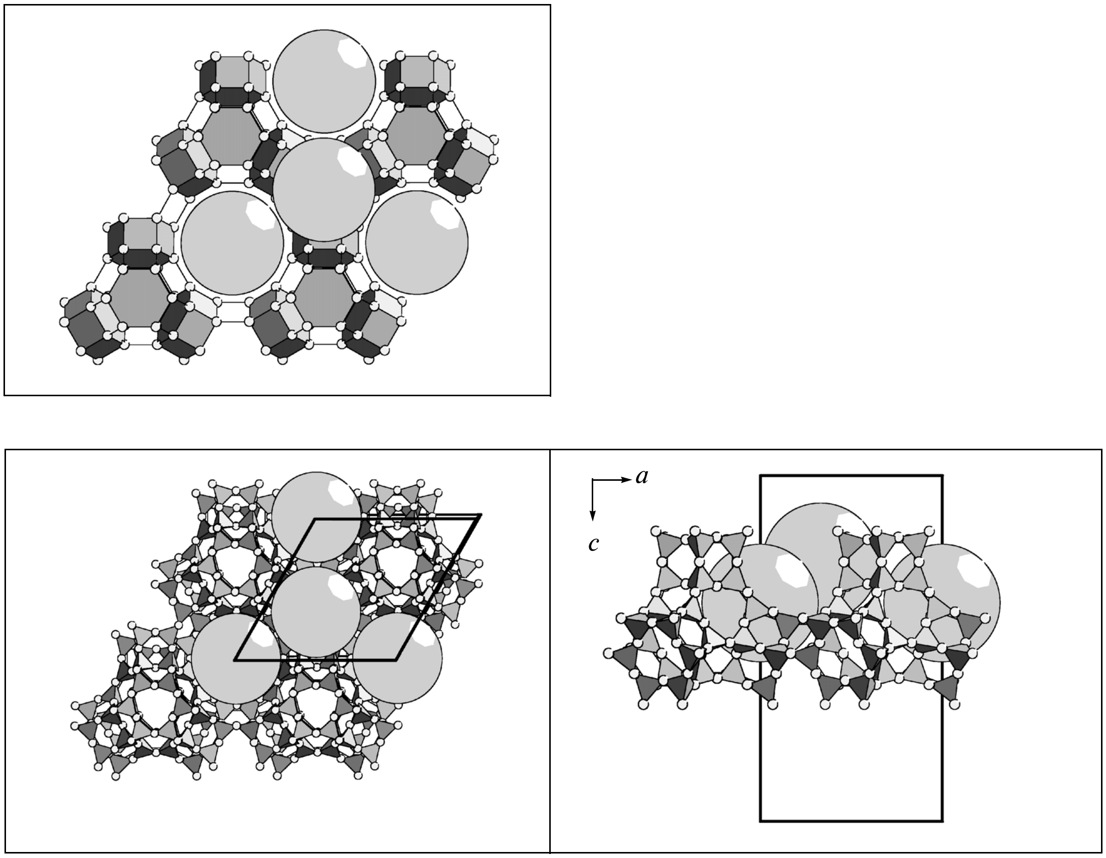


Fig. 12. 18C6,Na-EMT. A microlayer of two primary chains. Upper panel: supraclusters imaged as graphs. Lower panel: the same as suprapolyhedral clusters (two projections).

correspond to the minimal value of the elementary growth step.

The multiple 3D condensation of structural blocks 2 × 2 × 2, which are complementarily connected at their boundaries, leads to the self-assembly of 3D macrostructure. The arrangement of 18C6 template molecules in the 3D framework corresponds to the graphite 2D network.

The cluster self-assembly model of 3D structures from supraclusters T48 is capable of explaining the morphogenesis of EMT single crystals with the formaiton of hesagonal prisms (Fig. 7).

Ca,Ba-TSC Zeolite Structure Type

The mineral Tschörtnerite, with framework TSC, has a complex chemical composition

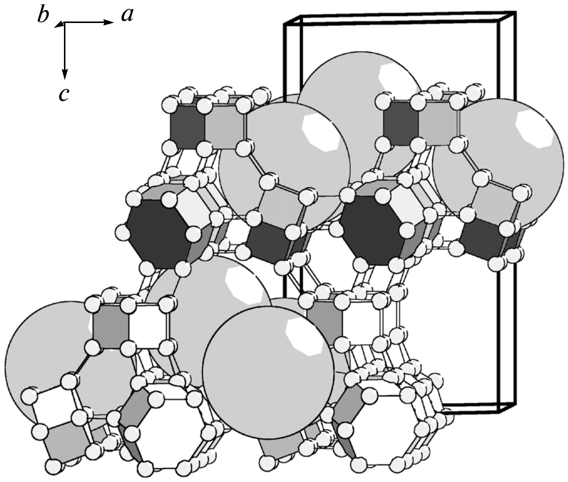


Fig. 13. 18C6,Na-EMT. A microframework of two microlayers. Supraclusters imaged as graphs.

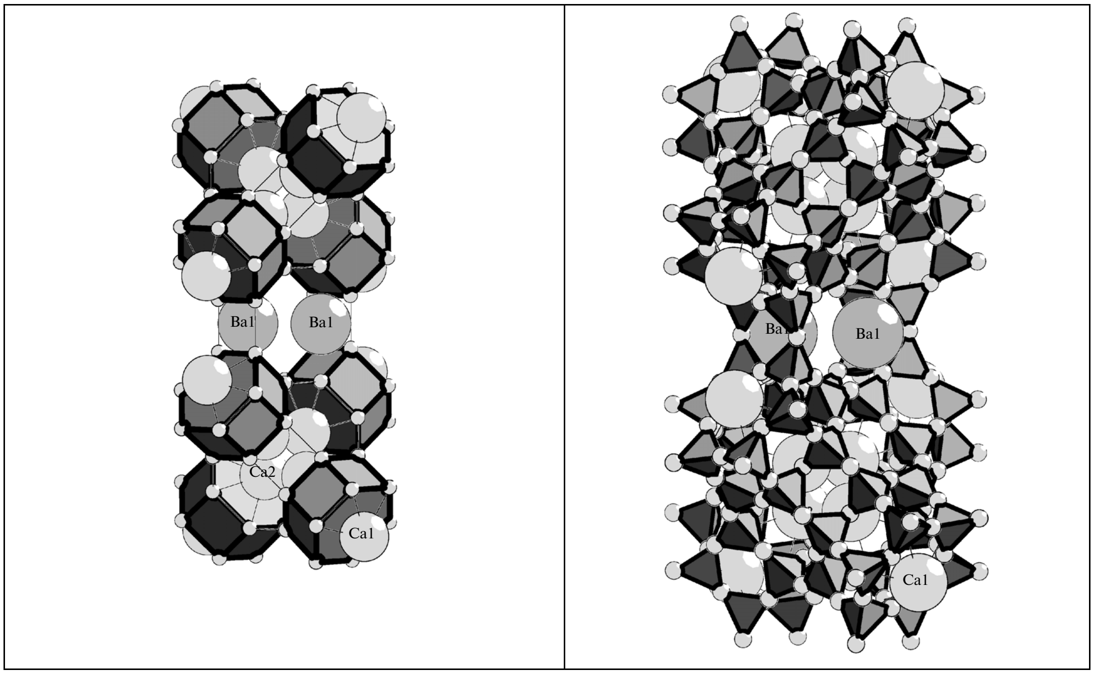


Fig. 14. Ca,Ba-TSC. A primary chain of two supraclusters K48. Ba(K,Sr) spacer cations randomly fill positions between supraclusters K48. Left-hand panel: supraclusters imaged as graphs. Right-hand panel: the same as suprapolyhedral clusters.

$Ca_4(K,Ca,Sr,Ba)_3Cu_3(OH)_8[Si_{12}Al_{12}O_{48}] \cdot xH_2O$, where $x \geq 20$ [18], and exists as well-faceted cubes with sizes up to 0.15 mm [18]. No synthetic analogues of TSC have been prepared.

Precursor cluster. Precursor supracluster T48 in the crystal structure retains point symmetry $\bar{4}3m$, the center of the supracluster in the unit cell is in positions 8*c*. The topological type of basal 3D network for precursor clusters T48 corresponds to the cubic polonium structure with CN = 6 (Fig. 7).

Primary chain. The self-assembly of TSC primary claims occurs in the direction of axis *a*. Complementary connection occurs over local regions, which are four vertices of tetrahedra of each supracluster K48 (Fig. 14).

Microlayer. Microlayer self-assembly occurs through connection of parallel lying short chains, each built of two supraclusters T48, in plane (001) (Fig. 15) by the identity mechanism, as for the primary chain assembly.

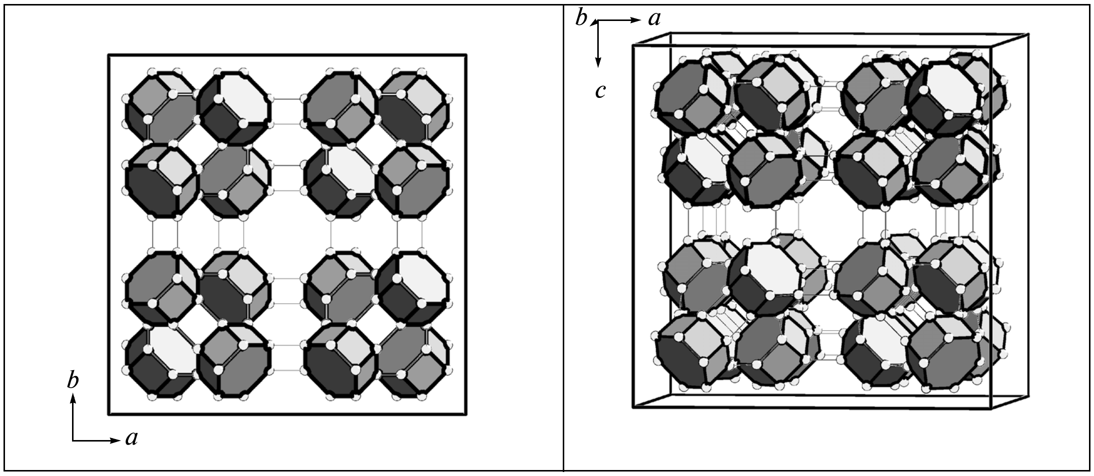


Fig. 15. Ca,Ba-TSC. A microlayer (left) and a microframework (right).

Microframework. A microframework is formed by connection of two microlayers along axis c (Fig. 15). The elementary growth step height is $a = 31.62$ Å. The resulting single crystal acquires the form of a cube (Fig. 7), and growth macrosteps on a cube face have rectangular shapes [18].

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