Structural Chemistry of Metal Inorganic 3D MT Frameworks. Templat ed Nanoclusters—Precursors Ga₂(PO₄)₂F₂ and Ga₂(PO₄)₂(HF)₂ and Self-Assembly of Crystalline Gallophosphate Structures (NH₄)₂[Ga₂(PO₄)₂F₂](KTP-Type) and (NH₄)₂[Ga₂(PO₄)₂(HF)₂](p-KTP-Type)

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Abstract—The article discusses the structural chemistry of metal inorganic microporous 3D MT-frameworks of M-octahedra and T-tetrahedra. Geometric and topological simulation has been applied to topologically different suprapolyhedral M₂T₂ clusters of two octahedra and two tetrahedral, with the hierarchical structure presented in the form of two-colorable graphs. The obtained data have been used during the search for clusters-precursors of metal inorganic microporous 3D MT-frameworks in the arranged database of crystalline MT-structures (13455 compounds, ToposPro program package). For gallophosphates of close chemical composition (NH₄)₂[Ga₂(PO₄)₂F₂] (KTP-type), (NH₄)₂[Ga₂(PO₄)₂(HF)₂] (p-KTP-type), the complete 3D reconstruction of the cluster self-assembly of crystalline structures has been performed: nanocluster—precursor S⁰₁—primary chain S⁵₁—microlayer S⁴₁—microframework S₃₁. The simulation involves the methods of combinatorial topology analysis based on plotting a basic 3D net of zeolite in the form of a graph, the nodes of which correspond to the position of the gravity centers of clusters—precursors Ga₂(PO₄)₂F₂ for KTP and Ga₂(PO₄)₂(HF)₂ for p-KTP. Both for KTP and for p-KTP the same type of crystal forming 2D nets 33344 + 3344 (1:1) have been set. Various variants of the complementary bonding of the 2D nets led to the formation of basic 3D nets with CN = 10 (KTP) and 8 (p-KTP). For the first time the functional role of NH₄ clusters—templates, which form hydrogen bonds with the O and F atoms and which fix the relative position of the two Ga₂(PO₄)₂F₂ and Ga₂(PO₄)₂(HF)₂ clusters, has been considered.

Keywords: metal inorganic 3D MT-frameworks, self-assembly of crystalline structures, templated nanoclusters—precursors, gallophosphate structural types (NH₄)₂[Ga₂(PO₄)₂F₂] (KTP-type) and (NH₄)₂[Ga₂(PO₄)₂(HF)₂] (p-KTP-type)

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INTRODUCTION

Crystalline structures of micro- and mesoporous zeolites—alumosilicates with tetrahedral 3D T-frameworks (T — AlO₄, SiO₄) and their structural analogs (alumophosphates, gallophosphates) for a long time were the subjects of detailed topological analysis at the suprapolyhedral level [1–10].

The possible combinatorial assembly models of zeolite crystalline structures of suprapolyhedral clusters templated with atoms of alkaline and alkaline earth metals are described in [4] in the context of the cluster SBU-model of the structure of zeolite frameworks (where SBUs are the secondary building units composed of PBUs, the primary building units in the form of T-tetrahedra).

All topological types of 225 zeolite frameworks can be combined in the families depending on the type of assembly clusters—precursors Tₙ (where n is the number of T-tetrahedra), forming packages during the self-assembly of crystalline structures. The most abundant is the crystalline chemical family of zeolites with the cluster—precursor T₁₂ of 12 bound T-tetrahedra (in the form of a hexagonal prism t-hpr), which, according to [4–10], is an assembly cluster for 11 types of 3D T-frameworks of zeolites.

The structural chemistry of metal inorganic microporous 3D MT-frameworks of zirconium sili-
cates of M-octahedra and T-tetrahedra was discussed in [11–14]. In terms of topological types of clusters—precursors, participating in the self-assembly of crystalline structures, 17 types of framework structures A, Zr-silicates (A = Li–Cs) in [12–14] were relegated to three homological series based on four-polyhedral cyclic $M_2T_2$ clusters, six-polyhedral cyclic $M_2T_4$ clusters, and four-polyhedral clusters of the MTMT and MTTM chain type. The work [13] for the first time analyzed templating the cyclic clusters $M_2T_4$ with atoms of alkaline (A) and alkaline earth (B) metals, and the interrelation between the chemical composition of nanoclusters—precursors and the composition of microstructures of A/B, Zr-silicates (A = Na, K; B = Ca, Sr) was established.

The family of metal inorganic microporous 3D MT-frameworks, in addition to the aforementioned zirconium silicates, also includes numerous crystalline structures of silicates and phosphates of polyvalent metals $M = M(3+), M(4+), M(5+)$, and $M(6+)$, which are obtained using alkaline and rare earth metals, as well as inorganic and organic molecules, as templates. Table 1 summarizes the chemical composition of the MT-structures of gallophosphates [15]. It should be noted that the majority of them were obtained in the last 15 years. In addition, at present more than 100 MT-structures of aluminophosphates were investigated [15]. In total, 2020 metallic phosphates, including all possible types of molecular, chain, layer, and framework MT-structures, have been studied [15]. It is possible to assume that the framework 3D MT-structures of aluminophosphates and gallophosphates are formed both with the participation of clusters—precursors, established previously for zirconium silicates, and new topological types of clusters—precursors, the structural models of which are discussed in this work.

This work performs the geometrical topological simulation of topologically different $M_2T_2$ suprapolyhedral clusters of two octahedra and two tetrahedral, with the hierarchical structures presented in the form of two-colorable graphs.

A search for local $M_2T_2$ fragments was performed in the created database of crystalline MT-structures, composed of 13455 compounds included in ICSD [15], by means of the ToposPro program package [16], which enables multipurpose investigation into crystalline structures in the automatic mode, using the pre-