Applied Topological Analysis of Crystal Structures with the Program Package ToposPro

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ABSTRACT: Basic concepts of computer topological analysis of crystal structures realized in the current version of the program package ToposPro are considered. Applications of the ToposPro methods to various classes of chemical compounds—coordination polymers, molecular crystals, supramolecular ensembles, inorganic ionic compounds, intermetallics, fast-ion conductors, microporous materials—are illustrated by many examples. It is shown that chemically and crystallographically different structures can be automatically treated in a similar way with the ToposPro approaches.
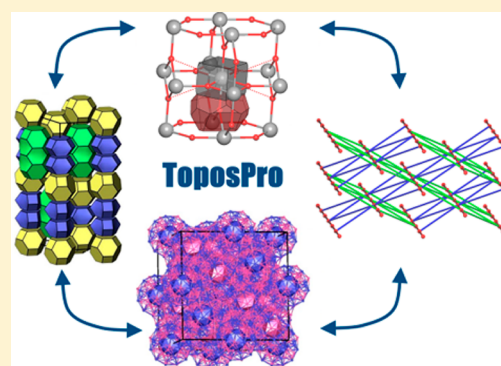
1. INTRODUCTION

The crystallographic databases—a lot of answers...but what are the questions?

—W. D. C. Motherwell (rephrased)

The above epigraph describes a survey of the development of the Cambridge Structural Database (CSD),[1] the largest electronic crystallographic database in the world. We have just replaced "CSD" by "crystallographic databases" and "450,000" by "a lot of" that extends the number of "answers" but retains the general meaning of the original quote: the worldwide crystallographic databases (CSD, Inorganic Crystal Structure Database, Pearson's Crystal Data, CrystMet, Protein Data Bank) have accumulated a huge amount of information, but the tools still have to be created to elucidate the regularities and relationships beyond these data.

Recent achievements in crystal engineering and materials science show the importance of data mining[2] to plan the design of new extended architectures with predetermined properties. At the same time, a question remains unanswered: how can deep regularities be derived from the standard crystallographic data, accounting for the fact that these data discard almost all information on the crystal electron density except the positions of its maxima (centers of atoms)? Crystallochemical analysis (i.e., the search for chemical relationships in crystallographic data) still consists mainly in studying geometrical characteristics of chemical structures (bond distances, angles, coordination polyhedra, etc.) and relating physical–chemical parameters (e.g., bond strength[3]). This *geometrical* analysis has proved its fruitfulness for a century of development, starting from first

structure determinations, but now it has probably reached the limit. Another way to obtain new knowledge from the standard crystallographic data is to explore the topological structure of the crystal space. For this purpose, one has to restore the connectivity between atomic domains and to study the properties of the resulting periodic graph,[4–6] Voronoi partition,[7] tiling,[8,9] minimal surface,[10,11] or entanglement.[12] This *topological* analysis originated from Wells,[13] but got faster development only in the last 10–15 years thanks to new mathematical methods, electronic databases, and computer algorithms and programs.[14–17] This paper concerns the methods of crystallochemical topological analysis implemented in the program package ToposPro. Special stress will be on the methods for mining the information to be valuable for experimental chemist.

2. EXPERIMENTAL SECTION

2.1. The Program Package ToposPro: Destination and General Overview. The program package TOPOS has being developed since 1989; at present, the Windows version 4.0 is exploited and distributed for free (http://www.topos.samsu.ru).[18,19] Now we change its name to ToposPro because of deep improvements made in the last years. Two main principles characterize the ToposPro philosophy as follows.

Objectivity. Processing crystallographic data should be as much independent of a human as possible; the crystal structures of any chemical nature and complexity should be analyzed with universal
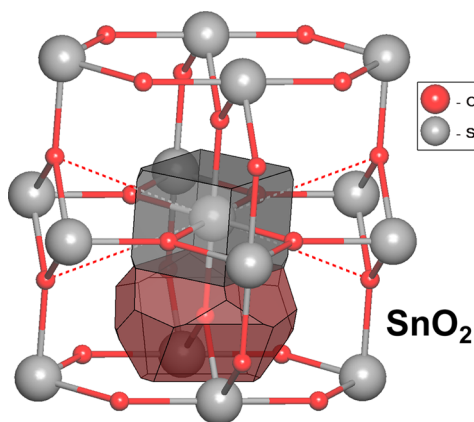
algorithms. This principle declares an alternative to traditional visual crystallochemical analysis: a crystal structure should be treated with formal computer procedures, and the structure images should be used only to illustrate the results, not as a source for conclusions. For example, when exploring microporous structures, a researcher should consider in the same scheme inorganic zeolites built with ion-covalent bonding, metal−organic coordination frameworks, or supramolecular architectures assembled with H-bond, specific, or van der Waals contacts. Moreover, the cages and channels in such structures should be separated with a universal algorithm, not with the motto: "I see it in that way."

Completeness. All available data should be considered while searching for or checking new regularities. The situation is inadmissible when one draws the conclusions after analyzing only a few compounds, ignoring hundreds or thousands of crystal structure determinations related to the problem under consideration. To apply this principle one has to implement new computer methods for crystallochemical analysis of large amounts of diverse crystallographic data in an automated mode.

The first principle is provided in ToposPro with a set of applied programs, unique algorithms, and methods of crystallochemical analysis. The second principle is realized as a database management system (DBMS) that supports various kinds of crystallographic databases and allows the researcher to compose his own data samples for a subsequent computer analysis. DBMS is integrated to the applied programs with a user-friendly interface.

All ToposPro methods can be subdivided into two groups: *geometrical* and *topological*. The first group is realized in the programs DiAn and IsoCryst and covers routine geometrical calculations (distances, angles, RMS planes, etc.) as well as visualization of crystal structures. The second group includes a number of procedures for studying the connectivity properties of the whole crystal space; they gave origin to the name TOPOS, thus declaring the main destination of the package. Most of the topological procedures are gathered in the programs AutoCN and ADS. One more set of methods, being formally geometrical, connects these two groups together. These are the methods of the program Dirichlet intended for construction of the Voronoi partition of the crystal space. They are described in detail in a special review[7] and require merely the initial crystallographic data to restore the crystal space connectivity. The crystal space is represented as a union of convex polyhedral atomic domains, and any face of any domain is shared between strictly two domains (Figure 1). Thus, any Voronoi polyhedron face corr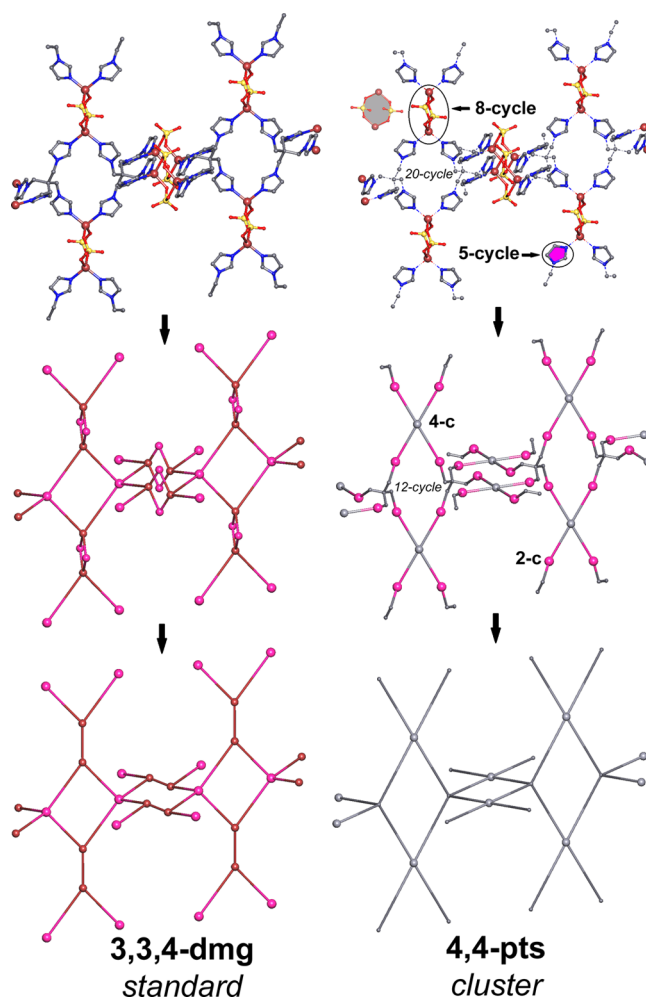esponds to an atomic contact to be classified as valence, nonvalence (H bond, specific, or van der Waals), or not bonding according to additional geometrical criteria.[18] Having the crystal space connected in this way we can apply the ToposPro topological methods.

2.2. Main Topological Parameters of Crystal Structures and Their Analysis.

When a chemist talks about *topology*, he rarely defines the term strictly.[22] At the same time, following the mathematical definition of topology, this term being applied to a chemical structure means just a set of chemical bonds or other links between structural groups (atoms, molecules, residues). Thus, any parameter that characterizes the properties of this set can be considered topological. In this part, we briefly discuss the topological parameters, most important for crystal chemist, as well as the methods of their analysis implemented into ToposPro.

Any chemical structure can be represented and analyzed in quite different ways depending on the structural groups and type of bonding under consideration. To describe any representation we use a chemical graph, whose vertices and edges correspond to the structural groups and links between them. In the case of an infinite periodic structure, the graph is called (periodic) *net*.[6] In Figure 2, two possible representations of the crystal structure of $[(\mu_4\text{-timm})_2\text{Zn}_4(\mu_2\text{-SO}_4)_4]\cdot4\text{H}_2\text{O}$ (timm = tetrakis(imidazol-1-ylmethyl)methane) {CUYTIA}[23] are shown; they will be discussed in detail below.

Net Elements. To characterize the overall net topology, several kinds of indices are used; these indices are based on finite elements of

Figure 1. Voronoi polyhedra of tin and oxygen atoms in the crystal structure of cassiterite SnO_2 {184420}[20] [hereafter the ICSD Collection Codes (numbers) or the CSD Reference Codes (letters) are given in braces]. The common face of the Voronoi polyhedra corresponds to the valence contact Sn−O. Four dotted lines show *indirect* contacts Sn−O (cf. ref 21) corresponding to small triangular faces of the Voronoi polyhedron (the lines of the contacts do not cross the faces) and assigning to no interatomic interactions.

Figure 2. Standard (left) and cluster (right) representations of the crystal structure of $[(\mu_4\text{-timm})_2\text{Zn}_4(\mu_2\text{-SO}_4)_4]\cdot4\text{H}_2\text{O}$ (timm = tetrakis-(imidazol-1-ylmethyl)methane) {CUYTIA}. The corresponding underlying nets are 3,3,4-coordinated **dmg** and 4,4-coordinated **pts**. Only one net of the 2-fold interpenetrated motif is shown.
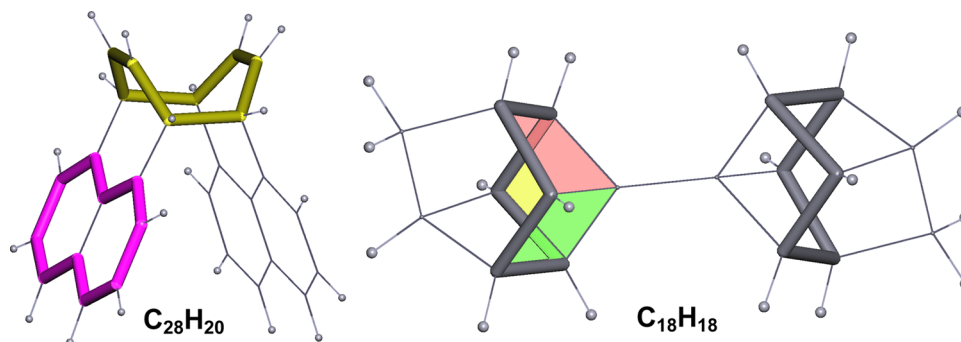
Figure 3. (Left) A 10-cycle [sum of two 6-cycle] (magenta) and strong 8-ring (yellow) in 3,4,5:8,9,10-dinaphtho-tricyclo(5.3.2.2^{2,6})tetradeca-11,13-diene $C_{28}H_{20}$ {BAPBID10}; (right) two weak 6-rings (gray) in 1,1'-bipentacyclo(5.2.0.0^{2,6}0^{3,9}0^{5,8})nonane $C_{18}H_{18}${JAJVOF} that are the sum of three strong 4-rings (filled red, green and yellow) with a common carbon atom.

the net that can be chemically interpreted. A *cycle* is any loop of bonds without self-crossings. A *ring* is a cycle that is not a sum of two smaller cycles. For chemistry most important is the *strong ring*, which is a cycle that is not a sum of *any* number of smaller cycles.[6] Strong rings can be considered as "primitive" cycles, from which all larger cycles can be built by summation. For example, in polycyclic hydrocarbons (up to a graphite monolayer) the benzene ring can be considered strong. In particular, 3,4,5:8,9,10-dinaphtho-tricyclo(5.3.2.2^{2,6})tetradeca-11,13-diene molecule[24] contains seven strong rings (four 6-rings and three 8-rings), while in 1,1'-bipentacyclo(5.2.0.0^{2,6}0^{3,9}0^{5,8})nonane molecule[25] there are weak 6-rings that can be represented as sums of three strong 4-rings (Figure 3).

The local topology of net is also characterized by the *coordination figure* that is formed by the nodes B_i adjacent to a particular node A; the number of B_i is equal to the coordination number of A.

In a 3-periodic net, strong rings envelop three-dimensional closed cages (*tiles*) that form a division of the crystal space (*tiling*). The number of different tilings in the net is infinite, but one can separate the minimal cages (*natural tiles*) that are not sums of smaller tiles and build the unique space division called *natural tiling*.[9] The faces of natural tiles are the so-called *essential rings*[8] that form a subset of the strong rings. The strict algorithm for constructing natural tiling was proposed and realized in ToposPro[8] (Figure 4).
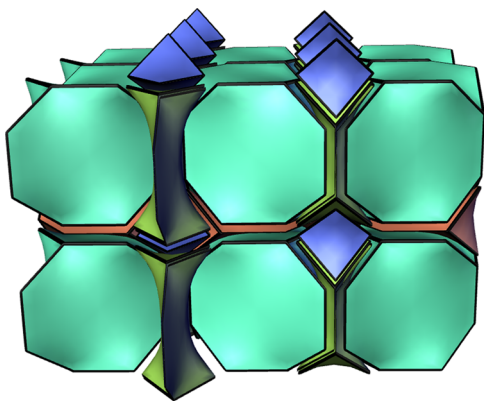
Figure 4. Natural tiling for the crystal structure of thomsonite $NaCa_2(Al_5Si_5O_{20})(H_2O)_6$ {61166}. The picture is drawn with the 3dt program[26] using an input generated with ToposPro.

To characterize the topology of a local part of the net one can examine the shell graph SG_n, which is based on a net node and includes n coordination shells circumscribed around the node. The shell graph imitates the growth of the structure from a selected center (Figure 5). An important ToposPro feature is the capability to search for a particular shell graph (and in general for any finite graph) in infinite nets of any complexity (see below the analysis of intermetallics).

Net Indices. The finite net elements are the base for quantitative parameters of the net topology, i.e., the net indices. The ordered sequences of sizes of minimal cycles and rings form *point symbols* and *vertex symbols*, respectively.[27] If one considers not only minimal cycles but also all cycles up to a particular size, one obtains a *cycle sequence*.[28,29] The set of numbers of nodes in the shells of the shell graph forms a *coordination sequence*. The natural tiling is described by the *tiling signature*, which enumerates all nonequivalent tiles written as their *face symbols*.[27] Any of the indices can be considered as a numerical parameter of the net topology. For example, $AuNb_3$ has a binodal 12,14-coordinated net. Nb and Au atoms in this net have point symbols $(3^{36}4^{42}5^{13})$ and $(3^{30}4^{30}5^6)$, respectively; the coordination sequences for the first 10 shells of the Au atom are given in Table 1. ToposPro uses a combination of coordination sequence, point, and vertex symbols that is sufficient to distinguish almost any net occurred in crystal structures. Any net has its unique name; although there is no conventional nomenclature so far, the most useful is the RCSR nomenclature,[16] which uses three-letter symbols for the net names (see examples below).

Topological Representations. The concept of structure representation is the keystone of the topological analysis with ToposPro. The most general approach to the crystal structure description is to consider all atoms and all (even weakest) links between them. The resulting topology is maximal; all other topologies of the structure can be derived from this topology. This topology corresponds to the *complete representation*, any other representation with a derived topology is *partial*. A partial representation is always simpler than the complete one since the number of vertices/nodes and/or edges of the corresponding graph (net) is smaller than in the complete representation. Among all partial representations, we distinguish the *standard* one that often corresponds to the most common way of interpreting crystal structures of a given kind by crystal chemists (see the examples below and Table 2).

Any partial representation can be generated by a *simplification procedure*. Although there is in general infinite number of partial representations, only a few of them have clear chemical meaning and can be obtained by a combination of the following simplification operations: (i) removing some nodes and/or edges, or (ii) contracting some nodes but keeping the graph connectivity. The first operation means ignoring some structural groups and/or bonds between them, while the second one represents some structural groups (molecules, coordination groups, residues, structural building units, etc.) in a simpler way, usually as their centers of mass. In fact, a simplification procedure is reverse to *decoration* of the net nodes with some polyatomic groups.[14] For example, in Figure 6 the simplified net of [(imidazole)$_2$Cd$_2$(μ_4-C$_2$O$_4$)(μ_2-C$_2$O$_4$)] {VAHTOO}[30] consists of cadmium atoms and centers of mass of the oxalate anions and imidazole molecules.

Another example is the H-bond pattern in the hydrazinium 5-oxo-4,5-dihydrotetrazol-1-ide crystal structure {YEKGUS}.[31] In this case, the structural groups are organic ions and the connections between them are formed by H bonds. Respectively, the sqc25 simplified net is
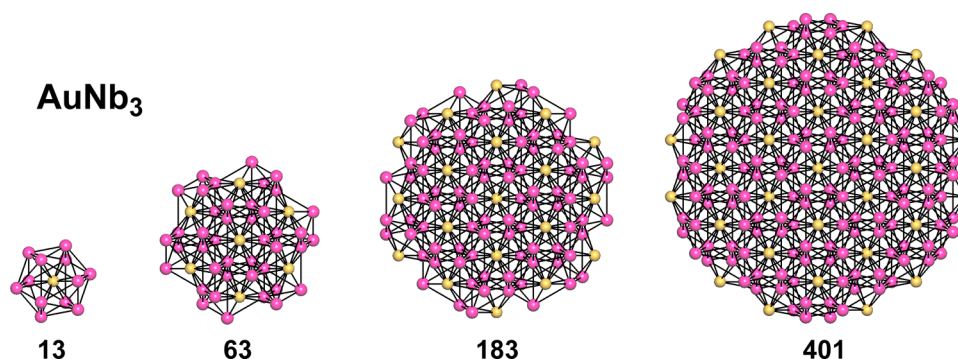
Figure 5. Shell graphs for an Au atom in the crystal structure of AuNb$_3$ {612203}. The numbers of atoms in the graph are indicated in the bottom.

Table 1. Coordination Sequences for Central Atom Au in Crystal Structure AuNb$_3$

shell number		1	2	3	4	5	6	7	8	9	10
number of atoms in shell		12	50	120	218	344	546	728	902	1212	1526
cumulative number of atoms		13	63	183	401	745	1291	2019	2921	4133	5659
cumulative number by atom sort	Au	1	15	51	101	169	331	531	737	1013	1435
	Nb	12	48	132	300	576	960	1488	2184	3120	4224

Figure 6. Original and underlying nets for the structure of [(imidazole)$_2$Cd$_2$(μ_4-C$_2$O$_4$)(μ_2-C$_2$O$_4$)] {VAHTOO}. The 2-periodic 3,4-coordinated underlying net belongs to the **mcm** isoreticular series.

Figure 7. A fragment of hydrazinium 5-oxo-4,5-dihydrotetrazol-1-ide (H$_5$N$_2$)$^+$ (CHN$_4$O)$^-$ {YEKGUS} and its binodal 6,6-coordinated *sqc*25 underlying net (green).

terminal imidazole molecules are excluded from consideration at this stage.

There are other types of chemically reasonable representations that can be generated from the graph of the structure in accordance with formal topological criteria. The *cluster representation* can be obtained by division of all bonds in the crystal structure to *inter*cluster and *intra*cluster. The following topological criterion is applied: any intercluster bond belongs to at least one small cycle of bonds, while all intracluster bonds belong to only large cycles. Chemically, this means that intercluster bonds form rather dense groups, while the intracluster bonds connect these groups together. ToposPro uses a simple condition to distinguish these types of bonds: if all $i = 1−n$ bonds are ordered by the size N_i of the minimal cycle to which they belong and there is such m that $N_m − N_{m−1} > 2$ holds, then all bonds with $i < m$ are assumed intracluster, while other bonds with $i \geq m$ are to be intercluster. For example, the cluster representation of CUYTIA as a net of [Zn$_2$(μ_2-SO$_4$)$_2$] dimers and timm molecules (Figure 2) can be obtained if the bonds belonging to the largest 20-cycles are considered as intercluster. This condition can be obeyed for different m, so several cluster representations can exist for the same structure. This representation can be considered as standard for coordination polymers that contain polynuclear complex groups or metal clusters.[32]

One more type of representation, the *edge net*, can be obtained by replacing the edges of the initial net with new nodes, and connecting the nodes in accordance with the connectivity of the edges of the initial net. A *partial edge net* is especially important, where only part of the edges of the initial net are replaced with nodes; for example, such kind of edge net corresponds to a packing of 1,3-propanediol dimers {QATTEK}.[33] While the standard representation of the structure as

composed of the ions centers of mass (H$_5$N$_2$)$^+$ (CHN$_4$O)$^-$ with the edges that mimic the H-bond pattern (Figure 7).

The topology of a partial representation is described by an *underlying net*, i.e., the net that reflects properties of the structure connectivity to be the most important for the task under consideration. Alternatively, the underlying net can be considered as the method of assembling the whole structural motif from the building units. If the underlying net contains 1- or 2-coordinated nodes, which correspond to terminal or bridge structural groups, as well as if there are isolated (0-coordinated) nodes outside the net, a *secondary simplification procedure* should be additionally applied to obtain the standard representation. As a result, the 0- and 1-coordinated nodes are removed, while the 2-coordinated nodes are contracted to edges of a new simplified net. Thus, the standard representation cannot be simplified more without changing the net connectivity. For example, in the VAHTOO underlying net (Figure 6), the centers of mass of the
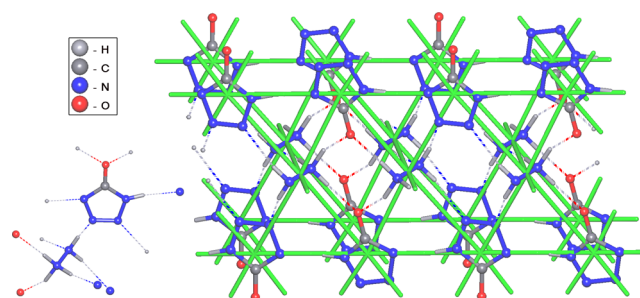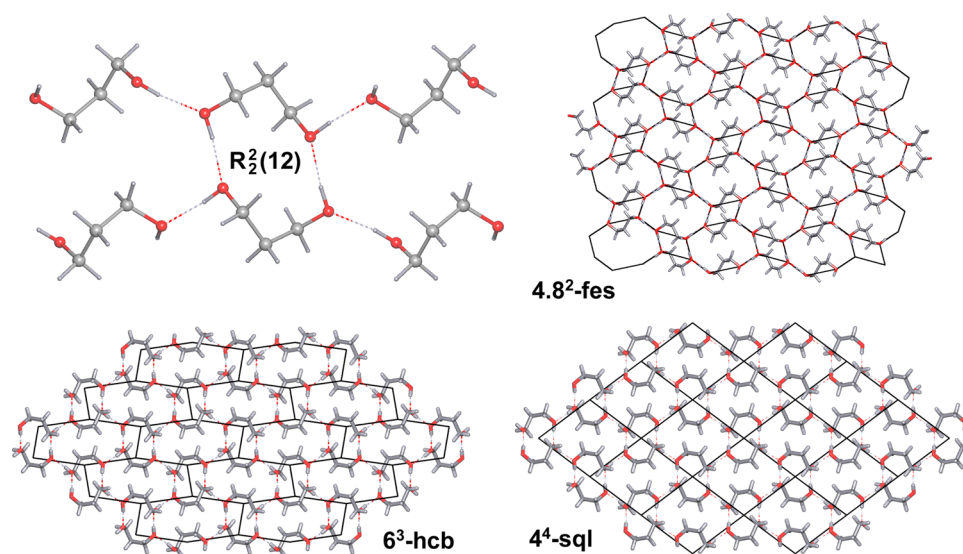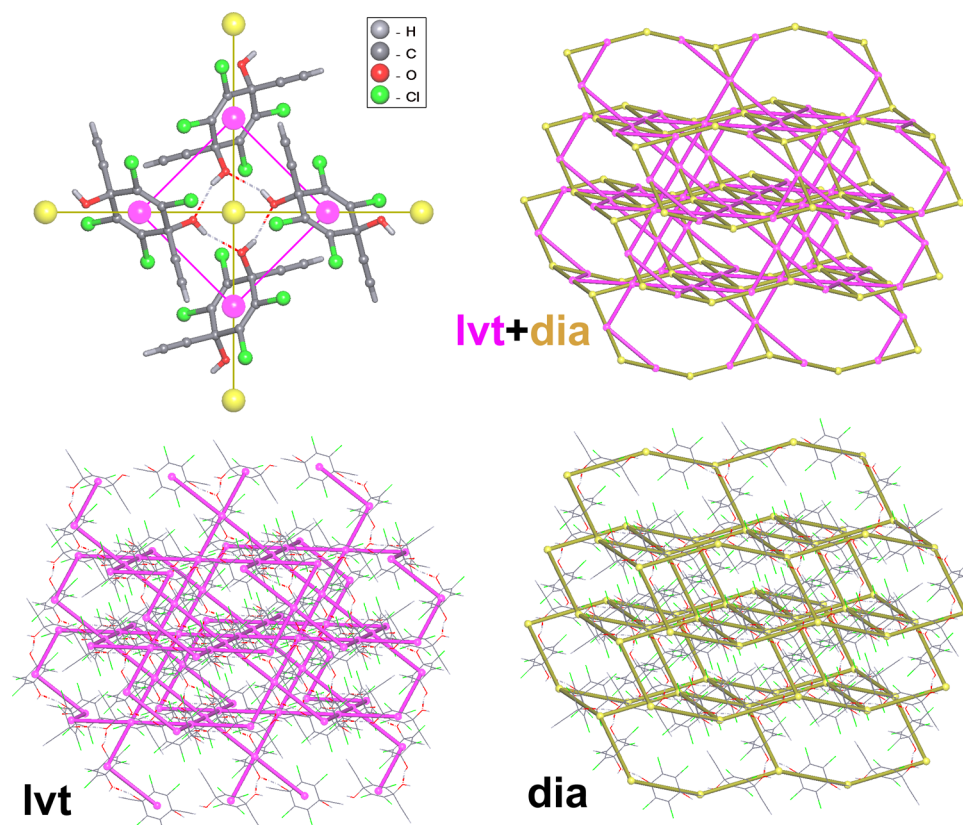
Figure 8. Crystal structure of 1,3-propanediol {QATTEK} showing the hydrogen bonded dimers and three possible representations: **hcb** underlying net corresponding to the standard representation; **sql** underlying partial edge net of dimers; **fes** underlying net of the hydrogen bonded atoms.


Figure 9. An H-bonded motif (left top) in the crystal structure of 2,3,5,6-tetrachloro-*trans*-1,4-diethynylcyclohexa-2,5-diene-1,4-diol {XEHKIE} in the standard representation (**lvt** net, left bottom) and as a partial ring net of H_4O_4 synthons (**dia** net, right bottom). Note that **lvt** net is a partial edge net for **dia** (right top).

the 1,3-propanediol molecules taken as a whole results in a honeycomb (**hcb**) underlying topology, the cluster representation of dimers gives rise to a square lattice (**sql**) topology. One more representation as **fes** is possible if the hydrogen bonded oxygen atoms are consider as nodes (Figure 8).

The *ring net* is constructed by placing new nodes in the centers of rings of the initial net and connecting them by new edges corresponding to the edges of the initial net shared by the adjacent rings. Similar to partial edge net, a *partial ring net* is formed from a

subset of all rings of the initial net. In particular, such kind of ring net describes the topology of a system of synthons. An example is shown in Figure 9; the H-bonded 2-periodic motif in the crystal structure of 2,3,5,6-tetrachloro-*trans*-1,4-diethynylcyclohexa-2,5-diene-1,4-diol {XEHKIE}[34] can be treated in a standard representation (the nodes of the underlying net coincide with the centers of mass of the molecules) with the **lvt** underlying net or as a diamondoid (**dia**) net of centers of H_4O_4 synthons consisting of four hydroxo groups. Another important
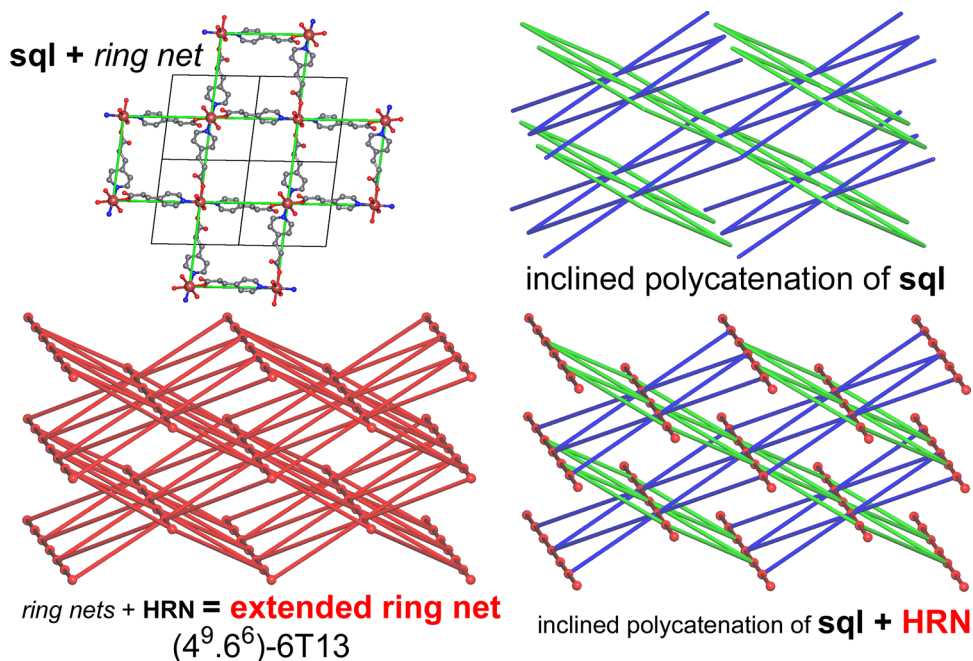
Figure 10. Associate **sql** ring net of the 2-periodic **sql** net in the crystal structure of Ni(*trans*-4-pyridyl acrylate)$_2$(H$_2$O)$_2$ {ODIZIK};[36] the inclined polycatenation (top right) generates 1-periodic Hopf ring net (in red bottom right) that together with the 2-periodic ring nets results in a 3-periodic 6-coordinated extended ring net (bottom left).

application of the ring net is in the analysis of entanglements (see below).

The concept of crystal structure representation is important to formalize the notion of "topology" and implement it into computer methods. This approach allows one to enumerate all chemically reasonable visions of the structure and decide which of them is important for the task under consideration. Thus, the motto: "I see it in that way" transforms to "I have studied all representations and I choose this one for those reasons."

The net indices characterizing the topologies of underlying nets are stored in the TTD (TOPOS Topological Databases) collection, which is an integrated part of TopsPro. Currently, this collection contains almost 80 000 topologies to be important for crystal chemistry, including those from other topological databases RCSR[16] and EPINET.[17] The TTD collection is being continuously updated with new topologies obtained from the releases of CSD, ICSD, and Pearson's Crystal Data, as well as from the authors of original structure investigations.

Entanglements. Ring net is a powerful tool to formalize one more topological feature of crystal structures, the entanglement of structural groups. Let us consider the entanglement that exists due to Hopf links between rings. One can construct an *extended* ring net, where additional edges connect the centers of rings in the Hopf pairs.

The extended ring net can be split into two subnets: the set of ordinal ring nets that characterize the adjacency of rings within the atomic nets of the entangled array and the nets of Hopf links (*Hopf ring nets*) that describe the entanglement topology. The periodicity n of the extended ring net coincides with the periodicity of the entangled array, while the ordinary ring nets determine periodicities m_i of entangling nets in the array: $\{m_i\} \rightarrow n$. The entanglements can be classified with the topologies of the Hopf ring nets; one can state that two structures are entangled in the same way if their Hopf ring nets have the same topology.[35] As example we illustrate in Figure 10 the ring net for the 2-periodic **sql** net in the crystal structure of Ni(*trans*-4-pyridyl acrylate)$_2$(H$_2$O)$_2$ {ODIZIK},[36] the inclined polycatenation that generates the 1-periodic Hopf ring net and the 3-periodic 6-coordinated extended ring net. Here the ring net is a net of centers of **sql** square rings and hence is also an **sql** net; the Hopf ring net is just a straight chain, which corresponds to the chain of catenating rings. The extended ring net being a sum of the 2-periodic **sql** ring net, and 1-

periodic chain Hopf ring net is a 3-periodic 6-coordinated net with the 6T13 topology.

Topologies of Local Atomic Configurations. Besides tools for analysis of overall topological properties of crystal networks, TopsPro includes procedures for exploring topology of finite atomic configurations: molecules, clusters, polynuclear complex groups, as well as their ensembles. These procedures are based on the unique TopsPro capability to search for a finite graph of any size in extended structures of any complexity.[37] For a description of local topology in coordination polymers, the notation[38] is used. Recently,[39] this notation was improved to describe molecular crystals. A number of applications of analysis of local topological features of crystal structures are considered below; establishing correlations between chemical composition of molecular species, their topological parameters, and the architecture of the whole crystal structure gives us a possibility to develop the first expert systems in crystal design.[40,41]

2.3. Applications to Various Classes of Chemical Compounds. The topological methods are still not widely used in crystallochemical analysis. One of the reasons, in our opinion, is that they seem not so useful for practical chemists as traditional analysis of interatomic distances or electron density. Below we consider main implementations of the concepts described above.

Overall Topology of Underlying Nets. Why do we need to determine the topology of the structure representations? The first reason is the taxonomy problem. Since the net topology is independent of geometrical distortion of the crystal structure, one can introduce the notion of *isoreticular series*[42] that is the set of crystal structures with the same topology of the underlying net. The taxon *topological type*[43f] can be applied to not simplified structures that have the same topology, but likely, different space-group symmetry, which is crucial for the *structure type* taxon.[44] This means that an isoreticular series can include several topological types, and in turn the topological type can include several structure types. When the underlying net coincides with the whole structure, i.e., when the structural units are separate atoms, topological type coincides with isoreticular series. For example, topological type as well as isoreticular series of AuNb$_3$ determined with the topological indices (Table 1) is **bet** (β-tungsten).

In recent years, a number of reviews of the overall topology of underlying nets in inorganic,[45] organic,[46] and metal−organic coordination compounds[43] were issued; most of them were performed

with ToposPro and the TTD collection. These studies have resulted in the appearance of two more ToposPro collections: Topological Types Observed (TTO) and Topological Types Relations (TTR).[40] The TTO collection contains the data on occurrence of underlying nets of a given topology in CSD and ICSD; the CSD Reference codes and ICSD Collection codes are used as references to the original crystallographic data. The standard representations used in the TTO collection depending on the nature of bonding are described in Table 2. The TTO collection also contains the information on cluster representations (if any), so the same structure can be described in different ways.

Table 2. Standard Representations for Main Classes of Crystal Structures in the TTO Collection

class of crystal structures	structural groups (nodes of the simplified net)	type of bonds within the structure unit	type of bonds between the structure units = edges of the simplified net
inorganic ionic compounds	metal ions, complex ions	valence	ionic
intermetallic compounds	metal atoms, metal clusters	metallic	metallic
porous structures	cages	valence	valence
valence-bonded coordination compounds	metal atoms, ligands	valence	valence
H-bonded coordination compounds	complex groups	valence	H-bond
organic crystals, supramolecular complexes	organic molecules	valence	any intermolecular[a]

[a]H-bonds, van der Waals, or other more specific secondary interactions as S···S, I···I, etc.

Having assigned the crystal structure to a topological type or isoreticular series, one can find all related structures just looking through the corresponding list of the TTO collection. The relationships found with this approach can be quite far from the chemical point of view because quite different groups of atoms can be assigned to the nodes of the underlying net (Table 2). For example, quite chemically different structures are based on the same **rtl** (rutile-like) underlying net: the 3-periodic $Zn(C(CN)_3)_2$[47] and the hydrogen bonded net of N,N,N',N'-tetra-amino-piperazindi-ium bis(azide)[48] (see Figure 11). Both are 2-fold interpenetrated. Since the underlying net shows the method of assembling structural units, this fact means that these structures are assembled in the same way.

Furthermore, the relationships can be expanded beyond the topological type or isoreticular series. The TTR collection includes relationships between underlying nets of different topology corresponding to different representations of the same structure in the TTO collection. Indeed, if a particular structure has both standard and cluster representations (cf. Figures 2 and 9), the corresponding underlying nets can be transformed to each other by simplification or decoration procedures, and, hence, their topologies are interrelated. It is important, that theoretically, the number of relations between nets is huge,[49] but the TTR collection stores only those that are observed in crystal structures and have clear chemical meaning.

One more reason to use the data on underlying nets is that the overall topology describes the long-range structure of a crystal irrespective of the space-group symmetry. This means that the same topology can be realized in different space groups and with strong distortions of the structure. At the same time, any net has its inherent combinatorial symmetry that always greater or equal to the crystallographic symmetry;[15,50] the combinatorial symmetry is described by an automorphism group. Not any space group can be assigned to the net but only that one which is a subgroup of the automorphism group. Thus, the knowledge of possible net topologies for a given chemical compound is an additional restriction when
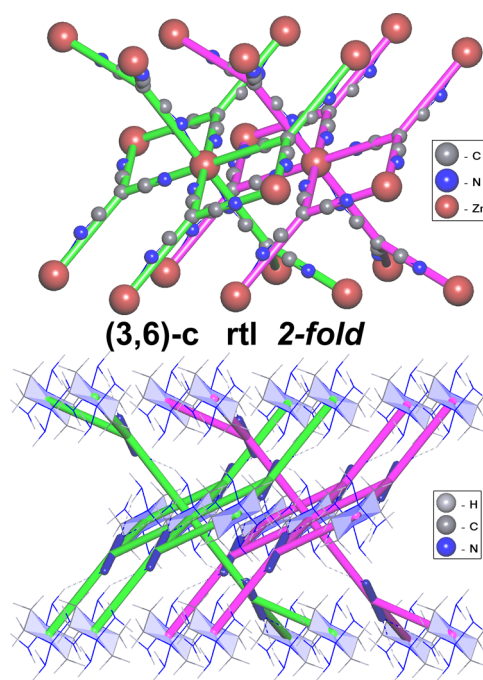
Figure 11. Rutile-like (**rtl**) 2-fold interpenetrating underlying nets shown by green and red sticks: (top) in $Zn(C(CN)_3)_2$ {JIHROH} (sp. gr. *Pmna*); (bottom) in N,N,N',N'-tetra-amino-piperazindi-ium bis-(azide) {TAPIPZ} (sp. gr. $P2_1/c$). In the bottom picture, the cations $(C_4H_{16}N_3)^{2+}$ and anions $(N_3)^-$ are shown as filled rings and blue sticks, respectively.

searching for possible extended architectures and an important point in crystal structure prediction.[40,41,51] The realizations of a given topology in various space groups can also be found with the TTO collection (Figure 11).

Entanglements in Coordination Networks. In recent years, a special interest was paid to the purposeful synthesis of entangled 1D, 2D, or 3D architectures. Thus, the number of interpenetrating 3D coordination networks obtained since 2004[43a] is twice more than before 2004.[43f] To predict what compounds can form entangled arrays, it is important to know the net topologies that admit entanglement. We applied ToposPro to find interpenetration in all 3D coordination networks and revealed that the number of isoreticular series for the interpenetrating arrays is much smaller than for single networks.[43f] It is still an open question why some topologies never occur in the interpenetrating motifs. A detailed analysis of entanglement types described as Hopf ring nets[35] could be a possible way of solving this problem.

Nonetheless, many entangled architectures are obtained by chance, and the authors of original investigations often miss the entanglement. Sometimes the crystal structures are indeed too complicated to reveal the entanglement if it is not expected. A routine analysis of entanglements with ToposPro right after the X-ray experiment could help to avoid such misses.

Local Topology of Coordination Polymers. Local topology of coordination polymers depends on coordination features of metal atoms and coordination types of ligands that are automatically determined in ToposPro as coordination formulas according to the Serezhkin's notation.[38] Recently,[40] we used ToposPro for the first time for analysis of coordination types of ligands in more than 10 000 2-periodic coordination polymers. Strong correlations between coordination formulas and overall topologies of the polymeric motifs were revealed. In most cases, a particular combination of coordination types of metals and ligands leads to a specified overall topology with a high probability (more than 90%). As a result, one more ToposPro collection, Topological Types of Ligands (TTL), was created that

contains information about occurrence and topological types of ligands.

Packings and Associates in Molecular Crystals. The standard representation of molecular crystals in ToposPro automatically leads to an underlying net where the nodes correspond to molecular centroids, while the edges describe the system of intermolecular bonds. This underlying net characterizes molecular packing and can be used to analyze subtle changes in the molecular arrangement. To build such representation, ToposPro distinguishes intra- and intermolecular contacts and contracts the groups of atoms united by intramolecular contacts into centroids, while the intermolecular contacts are transformed into the edges of the underlying net. For example, acetaminophen exists in three polymorphic modifications with different molecular packings that are reflected by different molecular coordination numbers (MCN), i.e., numbers of surrounding molecules in the packing, MCN = 12,[52] 14,[53] and 16[54] and different topologies of the whole packing (Figure 12). The automatic search allows one to get
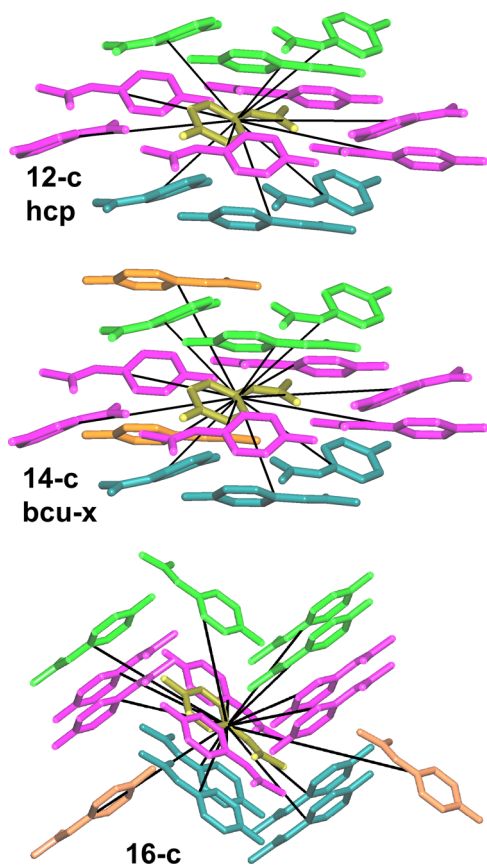

Figure 12. Polymorphs of acetaminophen $C_8H_9NO_2$ with different topology of molecular packings: (top) **hcp** with MCN = 12 {HXACAN24}; (center) **bcu-x** with MCN = 14 {HXACAN}; (bottom) unknown topological type with MCN = 16 {HXACAN01}. The central molecule is highlighted in yellow. The coordination figures are shown by black lines.

a distribution of molecular crystals on the packing topologies, and molecular coordination number 14 was found to be most frequent that corresponds to the body-centered cubic with extended coordination, the **bcu-x** underlying net.[55]

Similar to coordination polymers, supramolecular architectures reveal strong correlation between *molecular connection type* that characterizes the local topology of molecular ensembles[39] and the long-range topology of the system of intermolecular bonds. Recently,[41] we have shown that the sequence "molecular structure → molecular connection type → underlying topology of H-bond pattern" can be established with a high probability.

If intermolecular interactions are heterogeneous, i.e., along with van der Waals contacts there are stronger H bonds or other specific (halogen, $\pi-\pi$, etc.) interactions, the cluster representation corresponds to the packing of supramolecular associates. In this case, one should assign valence bonds as well as strong intermolecular interactions to "intramolecular", while van der Waals contacts remain "intermolecular". With this information, ToposPro squeezes the whole supramolecular associates into nodes of the underlying net that will characterize a packing of the associates. To obtain the standard representation, one just needs to change the type of specific bonds to "intermolecular" in the ToposPro options. The topologies of the two representations can be interrelated according to the TTR collection (cf. Figure 8).

Ion Packings in Inorganic Salts. The standard representation in inorganic salts can be constructed similar to that for coordination compounds if one considers metal cations as central atoms, while all other atoms form ligands. In this case, the ligands are counterions of any complexity, and the bonding between the structural groups can be assumed ionic (Table 2). The underlying net describes the packing of ions, or (since the complex anions usually contain a cation inside) the so-called *cation array*.[56] The model of cation arrays has been extensively developed in the past decades[56−58] and can be considered as alternative to the older model of inorganic compounds as a close packing of anions. The main idea of the model is that the cation array reproduces a motif of a simple salt or an intermetallic compound (Figure 13). According to the ToposPro philosophy, this means the
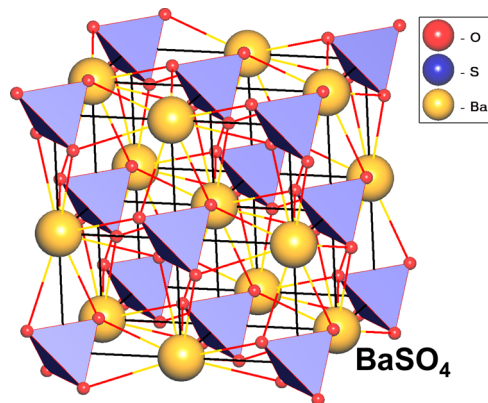

Figure 13. High-temperature form $BaSO_4$ {62368}[59] with a **pcu-b** underlying net (the NaCl structure type). The Ba^{2+} cations and the centers of the SO_4^{2-} ions correspond to Na^+ and Cl^- in NaCl or Ba^{2+} and S^{2-} in the isostructural BaS.[56]

coincidence of the underlying nets corresponding to the standard representations of the structures under comparison. A comprehensive analysis of oxoacid salts with ToposPro[58b] showed that such correspondences are quite common.

Cluster Models in Intermetallics. Quite another sort of cluster representation can be used to model the crystal structures of intermetallic compounds. In this case, the nature of chemical bonding is the same throughout the structure (Table 2), the topology of the framework is quite dense (all shortest cycles are small), so the criteria for separating clusters should be extended. These criteria were formulated in refs 19 and 60a as the principles of the *nanocluster model*: (i) the clusters are represented as shell graphs with centers (empty or occupied by high-coordinated atoms) at the most symmetrical positions; (ii) the clusters do not interpenetrate (they have no common internal atoms) but include all atoms of the structure. As a result, the structure is represented as a system of quasi-spherical onion-like nanoclusters, whose centers form an underlying net. The number of nanocluster models is finite for a particular intermetallic structure and can be enumerated with ToposPro. This approach gives the following new possibilities in crystallochemical analysis of intermetal-lics: (i) the cluster representation is much simpler than the initial
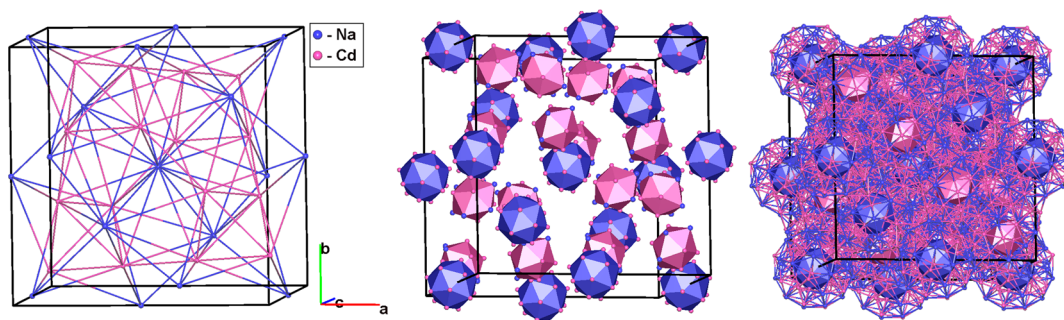
Figure 14. Nanocluster model of the NaCd₂ crystal structure {102030}:[62] (left) a MgCu₂-type (**mgc-x**) underlying net of centers of the nanoclusters; (middle) first shells of the nanoclusters (icosahedra and Friauf polyhedra); (right) the whole structure composed of two-shell 61-atom (Friauf-based) and 63-atom (icosahedron-based) nanoclusters.

structure and facilitates the structure description; (ii) new and unexpected relations can be established between crystal structures of quite different composition, metrics, and topology; (iii) the clusters are of nanosize (1−2 nm), often occur in many intermetallics, and can be found with the ToposPro procedure for searching for a finite fragment; this feature can help in building a bridge between nanosystems and crystals. Thus, the crystal structure of one of the Samson's "monsters", NaCd₂, can be represented as an ensemble of two-shell 61-atom and 63-atom nanoclusters (Figure 14) that were also found in other intermetallics. The centers of the nanoclusters are arranged in a MgCu₂-type (**mgc-x**) underlying motif.[61]

Natural Tilings in Zeolites and Fast-ion Conductors. The concept of natural tiling allows one to formalize the analysis of porous structures. With the algorithm implemented into ToposPro,[8] one can unambiguously determine all natural tiles and essential rings that correspond to minimal cages and windows of pores. Any larger cage can be represented as a sum of natural tiles, so the system of pores is comprehensively described with the natural tiling. It is important that natural tiles are constructed according to the topological criteria, and the resulting tiling is not sensitive to geometrical distortion of the structure. Therefore, this approach can be applied to any porous materials, or even to materials not referred to as porous, but possessing properties that depend on the void space, in particular, fast-ion conductors. Natural tilings are constructed for all zeolite-like frameworks[63] and listed in the Zeolite Framework Database (http://www.iza-structure.org/databases/). With the information on natural tilings, one can solve the following tasks:

(i) Determine the system of all voids and channels and represent them as a *dual net*, i.e., the net describing the topology of the void space. Then, applying additional chemical and geometrical criteria, one can discard some voids and channels to obtain a migration map for the particles under consideration. For example, in oxygen-framework fast-cation conductors one can consider only those dual net nodes and edges that correspond to tiles and rings formed by oxygen atoms and large enough to fit the mobile cations. The resulting migration map predicts the existence and dimensionality of conductivity[64] (Figure 15).

(ii) Search for similar porous structures that contain natural tiles of the same kind. The similarity can concern only the so-called *framework-forming tiles* that essentially determine the tiling topology or even to all tiles. In the latter case, we deal with isomeric *tile-equal* tilings, where topologically equal tiles are glued in different ways (Figure 16).

(iii) Analysis of natural tilings for hypothetical zeolites can give additional arguments for their stability and possible ways of synthesis. ToposPro has a special procedure to represent a zeolite framework as a packing of tiles where the tiles have no common T atoms but cover the whole framework. The resulting underlying net characterizes the topology of the packing. If a hypothetical natural tiling contains packing tiles typical for natural or synthetic zeolites and the topology of the packing is well-known; this could indicate such hypothetical zeolite to be feasible.[68] For example, the frameworks in 10 of the natural zeolites can be constructed as packings of hexagonal-prismatic
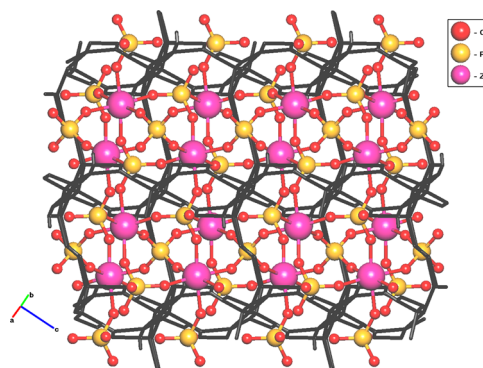

Figure 15. Migration map (in black) of Na⁺ cations in the Nasicon fast-ion conductor {64872}.[65]

cages (**t-hpr**); a number of hypothetical zeolites[69] can also be considered as **t-hpr** packings.[68] One of them (SFW) was obtained recently;[70] we can expect that others will be synthesized in the future.

3. CONCLUSIONS

The examples considered above demonstrate a diversity of applications of topological methods in crystal chemistry and design. The base of the ToposPro approach is the concept of structure representation and the corresponding concept of underlying net. In fact, to describe and solve any crystallochemical problem one needs (even implicitly) to determine what representation should be used and what physical meaning it has. It is the stage where the analysis remains human-dependent, and it is the crucial point of a correct application of ToposPro. Having the representation determined, the subsequent analysis is performed automatically in most cases. The unified methods of computer realization and processing of underlying nets allow the user to search for structural regularities by consideration of large samples of compounds or comparison of a particular structure with structures of quite other chemical composition and/or geometrical and topological properties.

Rapid development of the topological methods in crystal chemistry in the past 10−15 years promises further increase of their popularity. The theoretical background of the topological part of crystallography is still not as strong as the geometrical part, albeit essential efforts to improve the periodic graph theory were recently undertaken.[5] The new theory together with computer methods and software should facilitate asking the questions to which the electronic databases and expert systems might answer.[40] Moreover, the topological methods can be naturally combined with the quantum-mechanical
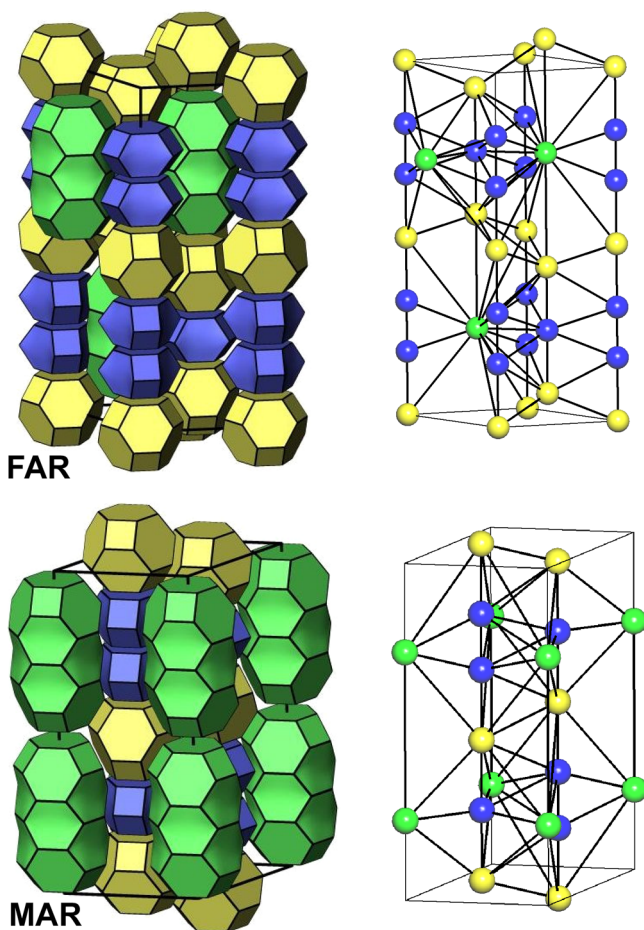
Figure 16. Natural tilings for zeolites FAR (farnesite) {155057}[66] (top left) and MAR (marinellite) {55429}[67] (bottom left) built of the same sets of tiles: **t-can** (blue), **t-sod** (yellow), and **t-lio** (green) and the corresponding underlying nets.

approaches[71] that can essentially improve the conclusions of the expert systems with quantitative estimation of structural parameters. Elaboration of such hybrid methods could become the main direction in which the topological methods will develop in the near future.

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Notes

The authors declare no competing financial interest.

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3586

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