1.4 Networks, topologies and entanglements

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1.4.1 Introduction

Making crystals by design requires both a detailed knowledge of the nature of the interactions involving the selected building blocks and also some general concepts concerning the types of the supramolecular extended arrays that could be generated by self-assembly, i.e. the possible target networks. The presence of suitable functional groups in an organic building block or the free coordination sites in a metal-based centre, all having well defined directions for interactions, can allow for some previsions about the resulting architecture, thus representing the fundamentals of the modern area of crystal engineering of networks. These points are treated in great detail in other parts of this book. However, in spite of this rather optimistic incipit, we are presently faced with many problems in the field and we are still far from being able to deliberately build networks with desired properties. A major difficulty arises from the range of possible different structures that can form in the self-assembly process, due to the occurrence of many, often unpredictable and subtle, concurrent factors.

Some advantage can derive from the analysis of related structures reported in the literature, searching for prototypical models that can fit the specific problem. The increasing number of networked species reported in the last years offers a rich variety of new structural types that continuously amplify our knowledge of these organic or metal-organic extended systems. From the structural point of view a great attention has been devoted to the rationalization and classification of the different topological types of single extended motifs [1] and to the categorization of the frequently encountered interpenetrating [2] and entangled [3] species. Indeed, the "network approach" or topological approach to crystal chemistry [4,5] is an important achievement in this area, as a useful tool for the analysis of network structures, in that it simplifies complex species to schematised nets, in order to make comparisons and identify packing trends that may help in the rational design of functional materials.

In what follows we will describe some approaches to the rationalization of these supramolecular systems proceeding in order of increasing complexity. We will deal first with the simplification of crystal structures, in order to carry out a topological analysis of the individual idealized networks.
Problems concerning the unambiguous assignment of the topology are presented, and topological approaches towards making crystals are described. Various types of entanglements of single motifs, including interpenetrated, polycatenated, Borromean, polythreaded and other networked arrays, will be then considered and classified.

1.4.2 Rationalization and simplification of the extended structures

A correct analysis of the crystal structures is fundamental in order to avoid misinterpretations, that can easily occur, about the network topology and, when present, the type and extent of the entanglement of distinct motifs. The rationalization of these, often complicated, structures implies a sequence of steps leading to the basic nets of linked nodes.

The steps, in general, can be summarized as follows: i) simplification process, ii) identification and separation of the individual motifs, iii) topological analysis of these motifs, and iv) topological analysis of the whole entanglement.

The simplification phase, previously exemplified by some authors [6], consists in the rather obvious operation of removing all the unnecessary elements that have no topological relevance, thus leaving only the essentials, represented by nodes and links (vertices and edges, respectively, in graph theory [7]). For instance, polyatomic nodes (like metal clusters or polyfunctional ligands) can be replaced by their baricentres.

The simplified model must be effectively representative of the connectivity of the real network. In some cases, however, this step leads to structural descriptions that are rather subjective in the selection of both the nodes and the connections (links) joining the nodes. Alternative rationalizations can be accomplished, that result in motifs of different topology, depending upon the choice of the chemical or/and mechanical bonds and the nodes of the architecture (see Figure 1.4.1) [8]. These "alternative" motifs, however, are not something unnatural; they reflect the possibility of consideration of a crystal from different points of view or at various levels of structure organization.

FIGURE 1.4.1

In coordination networks concurrent chemical forces are often operative, including coordinative bonds, hydrogen bond bridges, secondary bonds involving the anions, metal-metal interactions, \( \pi \)-interactions and others. Thus we are faced with the problem of deciding when a link is a topologically significant link. A current useful practice consists in assuming a level within this hierarchy of forces to be applied in the description of the net. For instance, we have previously observed [3] that in \([\text{Zn}(4,4\text{'-bipy})_2(\text{H}_2\text{O})_2]_(\text{SiF}_6)_2\) [11] the \(\text{Zn}(4,4\text{'-bipy})_2\) coordination sublattice is a
3D polycatenated array of two sets of inclined 2D square layers, but including also H$_2$O-SiF$_6$-H$_2$O hydrogen bond bridges that link the two different sets results in a more complex 3D single net having 4- and 8-connected nodes, with the peculiar feature of self-catenation (see later). Thus the insertion in a model of additional weaker interactions can have drastic effects, like changing the topology of the individual motifs, the type of entanglement or also the dimensionality of the whole array.

**FIGURE 1.4.2**

Mechanical bonds, like those shown in Figure 1.4.2, are responsible for the formation of the majority of the known extended periodic entanglements. A debatable point concerns the difficult distinction between rotaxanes and *pseudo*-rotaxanes. At the molecular level rotaxanes are characterized by the presence of bulky stoppers on the rods, that must inhibit dethreading, while *pseudo*-rotaxanes can be separated by chromatography or at high temperatures. Also some rotaxanes, however, can have low energy barrier to dethreading, so that the difference with respect to *pseudo*-rotaxanes remains a delicate problem and the boundary is not well-defined [12]. The extended polymeric analogues of these species present problems of similar nature; moreover, for them no experiment can be envisaged to differentiate the two situations.

We could, therefore, conclude that establishing the topology of these species is not only a formal process but rather an interplay between chemistry and mathematical theory. The process of simplification or abstraction that represents the passage from real objects to their idealized models needs chemical considerations. After simplification the problem remains exclusively based on a mathematical ground, and the successive process consists in the identification and classification of the topology of the individual motifs contributing to the entanglement. Their separation can be accomplished in a computer-aided process, whose output is a set of distinct "coloured" nets [13,14,15].

1.4.3 Topological classification of networks

1.4.3.1 Nomenclature for single nets: Schlafli and Vertex Symbols

The topological classification of an individual extended motif can be accomplished according to generally accepted criteria used in a variety of structural contexts, that are here described. Before of this, however, we want briefly mention the pioneering work of the researchers that have introduced...
the basic concepts for the rationalization, enumeration and classification of the extended crystal structures, using different approaches.

A fundamental contribution is represented by a famous series of articles and books on crystal chemistry published many years ago by A. F. Wells [4], who analysed and classified a great number of nets. He emphasized the importance to describe a crystal structure in terms of its basic topology: such a description not only provides a simple and elegant way of representing the structures but also evidences relations between structures that are not always apparent from the conventional descriptions. Wells introduced a method for the systematic generation of 3D arrays from 2D nets and described also many hypothetical motifs that were successively discovered within the realm of coordination polymers or of other extended systems. His results included a list of many simple nets described with only one kind of node (uninodal) or with two nodes of different connectivity (mainly binodal 3,4-connected).

The studies by J.V. Smith focused on the classification of zeolites and related materials with tetrahedral nodes of the TO$_4$ type [16]. He described a prolific number of frameworks that were discovered mostly by hand treatment, using systematic methods. Such methods include permutation of up-down linkages between identifiable two-dimensional layers in zeolites, as well as permutations of linkages between identifiable polyhedra.

An empirical search by O’Keefe [17] for uninodal four-connected nets resulted in the recognition of 168 distinct types (many of which unseen by Wells).

A thousand of uninodal nets were described over the years by Fischer, Koch and Sowa in their enumeration of homogeneous sphere packings, exploring systematically all crystal systems [18]. M. M. J. Treacy and coworkers have collected a hypothetical zeolite database, using a method that enumerates all possible 4-connected nets within each crystallographic space group given the number of unique tetrahedral vertices. The database contains $10^{10}$ graphs and is available at the website www.hypotheticalzeolites.net [19].

The different network topologies can be recognized following the graph theoretical approach. We can assign to the simplified 2D or 3D crystal structure a net, that is an infinite graph (or a periodic connected graph) described with translational symmetry in exactly two or three independent directions (2-periodic or 3-periodic nets) [20] and represented by nodes and links (vertices and edges, following the nomenclature of graph theory [7,21]). Figure 1.4.3 illustrates some common net topologies.

**FIGURE 1.4.3**
In the analysis of the topology of such nets we can look for a classification scheme that will allow to uniquely assign equal nets (up to isomorphism) derived from totally different crystal structures. Remember that the topology is not influenced by the metrical properties of the structure (angles, distances), so that a 4-connected diamondoid net is such even if highly distorted (the geometry around the nodes could be far from tetrahedral), and, obviously, also not dependent on the chemical nature of each node/vertex.

To make it easy we suggest here to follow the lower-case three-letter code nomenclature for nets proposed by O’Keeffe and coworkers [22,23] in the attempt to overcome a certain confusion in the field, due to the fact that some networks have been described with many names and symbols. For example the srs net observed for the Si atoms in the SrSi2 structure (see Figure 1.4.3) has been called (10,3)-a, Laves net, Y*, 3/10/c1, or labyrinth graph of the gyroid surface. The suggested nomenclature is designed to parallel the widely accepted upper-case three-letter codes used for zeolite frameworks [24]. Moreover, more than 1300 nets with these symbols have been collected in a very useful list described in detail at the RCSR (Reticular Chemistry Structure Resource) website of O’Keeffe group (http://reticularchemistry.net/RCSR/ [25]).

For most of the nets of fundamental importance in crystal chemistry, there are only a few different kinds of nodes (by "kind of nodes" we mean a set of vertices related by symmetry operations, including translations) and the assignment of the local topology for 2D or 3D nets is based on the analysis of the "circuits" (or cycles) at the angles of a node. A circuit is a closed path beginning and ending at each node, characterized by a size equal to the number of edges comprised in the path (3-circuit, 4-circuit and so on). Any two edges at a node define an angle, and with n-connected nodes [26] there are \( n(n-1)/2 \) such angles in a 3D net (but only \( n \) in a 2D simple layer [27]), for each of which we can find a large number of different circuits of different sizes.

A \( n \)-connected node can be identified by a Schlafli Symbol (short symbol or point symbol) of the form \( A^aB^bC^c... \), in which \( A < B < C < ... \) and \( a + b + c ... = n(n-1)/2 \), that represents the sizes \( (A, B, C...) \) and numbers \( (a, b, c...) \) of the "shortest circuits" contained at each angle. Thus for the 4-connected diamond net (dia), where all the shortest circuits are 6-cycles, the symbol is 66. For the 2D honeycomb and square-grid nets and for the 3D net of the 6-connected primitive cubic lattice (pcu), all uninode (i.e. containing a single type of node), the Schlafli Symbols are 63 [or (6,3)], 44 [or (4,4)] and 412.63, respectively.

For multinodal nets the Schlafli Symbols are grouped according to the multiplicity of the node in the unit cell; for example the net formed by the Si atoms in the silica form moganite (mog) is described as the 4-connected binodal net \( (4.6^4.8)\) because there are two crystallographic distinct nodes with multiplicity 2:1.
A special type of point symbol is assigned to uniform nets, i.e. nets in which the shortest circuits at each angle are all equal in size. It follows that the Schlӓfli Symbol for each node in a $n$-connected uniform net with circuits of size $A$ is $A^{n(n-1)/2}$. Examples include the series of 3-connected $10^3$ nets ($\text{srs}$, $\text{ths}$, $\text{bto}$, $\text{utp}$ and others), the 4-connected $6^6$ nets ($\text{dia}$, $\text{lon}$, $\text{gsi}$, $\text{lcs}$ and others) and also the binodal 3,4-connected $(8^3)_4(8^6)_3$ nets of $\text{C}_3\text{N}_4$ ($\text{etn}$) and $\text{Pt}_3\text{O}_4$ ($\text{pto}$).

The "point symbol" was extensively used in a slightly different typographic form by Wells [4], who was aware that this classification was far from being sufficient to unambiguously identify a net. In fact he added letters to the point symbol for assigning different topologies, as in the case of the well known 3-connected nets of the Si atoms in the SrSi$_2$ and ThSi$_2$ structures ($\text{srs}$ and $\text{ths}$ with the same Schlӓfli Symbol $10^3$), called (10,3)-a and (10,3)-b, respectively. Another case of ambiguity is given by the NbO net ($\text{nbo}$) and the arrangement of Si atoms in quartz ($\text{qtz}$), that have the same Schlӓfli Symbol $6^4.8^2$.

Given this inadequacy other descriptors are needed. To differentiate nets with the same Schlӓfli Symbol a modified version of it, the **Vertex Symbol** (VS, or long symbol introduced by O’Keeffe [1]) appears more useful. In a VS the size of the shortest rings at each angle is given with a subscript to denote the number of such rings. Solid state chemists define a ring as a circuit that has the property that there is no shorter path ("short cut") between any two vertices on the circuit than the shortest one that is part of the circuit (see Figura 1.4.4) [28].

FIGURE 1.4.4

Thus in the 3-connected $\text{srs}$ 3D net there are five 10-rings at each angle and the VS is $10_5.10_5.10_5$, and for the $\text{ths}$ net, with two, four and four 10-rings at each angle, the VS is $10_2.10_4.10_4$ (remember that for both nets the Schlӓfli Symbol is $10^3$).

In the case of 4-connected nets there are six angles at a node. The diamond net ($\text{dia}$) with two 6-rings at each angle has VS $= 6_2.6_2.6_2.6_2.6_2$. In 4-connected nets only, the angles are grouped into three pairs of opposite angles, and subject to that constraint, the smallest numbers are given first.

The feldspar structure ($\text{fel}$) contains a 4-connected net with two kinds of vertices both having the same Schlӓfli Symbol $4^26^38$, but different Vertex Symbols, $4.6.4.6.8.2.10_4$ and $4.6.2.4.8.6.6_2$. Here some 6- and 8-circuits have short-cuts and become 8- and 10-rings in the VS. Analogously we can now distinguish NbO, with VS($\text{nbo}$) $= 6_2.6_2.6_2.8.2.8_2$, from quartz, with VS($\text{qtz}$) $= 6.6.6.6.8_7.8_7$.

The Vertex Symbol of PtS (cooperite $\text{pts}$), that contains "square-planar" Pt and "tetrahedral" S centres with the same Schlӓfli Symbol $4^28^4$, allows also to differentiate the two nodes: Pt ($4.4.8_2.8_8.8_8.8_8$) and S ($4.4.8_7.8_7.8_7.8_7$). In this case the multiplicity of the 8-rings makes the
difference. More details on these symbols are given in references [1,21,29]. They are used also in the *Atlas of Zeolite Framework Types* [24a,b].

Not all the angles of a 4-connected net necessarily possess rings. When there is not a ring an asterisk is inserted in the VS. Thus for the 4–connected CdSO₄ net (the net of the Cd and S atoms, with the – O– links considered as edges, edS, Schläfli Symbol 6^8) the Vertex Symbol is 6.6.6.6.6₂.*.

Vertex Symbols can be computed for higher connectivities, but since the number of angles increases as the square of the coordination number, they soon become cumbersome; the Vertex Symbol for the 6-coordinated net of the primitive cubic lattice (pcu) is 4.4.4.4.4.4.4.4.4.4.4.4.*.*.*, and a 12-coordinated net has (12×11)/2 = 66 angles.

Also the Vertex Symbols, however, are unable to fully characterize nets. For example diamond and lonsdaleite (hexagonal diamond, lon) have the same VS = 6₂.6₂.6₂.6₂.6₂.6₂ and, therefore, other descriptors must be considered.

It is easy to introduce the "Coordination Sequence" CS(k) [1] of a node, defined as a sequence of numbers \((n_1, n_2, n_3, ..., n_k, ...\) in which the \(k\)th term is the number of nodes in "shell" \(k\) that are connected to nodes in "shell" \(k–1\). Shell 0 [CS(0)] consists of a single node and the number of nodes in the first shell [CS(1)] is the connectivity of the node (or more rigorously the coordination number of the vertex [26]). Another equivalent definition states that CS(k) gives the number of "topological neighbours" as the number of nodes that are \(k\) edges/links away from a given node. It follows that a \(k\)th neighbour of a node is one for which the shortest path to that node consists of \(k\) edges. Though there is no limit for \(k\) the CS is usually computed up to \(k = 10\). With this new descriptor we can now distinguish dia (CS= 4,12,24,42...) from lon (CS= 4,12,25,44...). The Coordination Sequences differ already at the third-neighbour, see Figure 1.4.5. We must say that CS alone is not sufficient, also because there are nets with the same CS but different VS (for example the zeolites Linde A lta and Rho rho).

**FIGURE 1.4.5**

For many years the structural analysis for assigning VS and CS was carried out by hand for simple nets but nowadays it can be performed computationally with the use of available computer programs like TOPOS [14,15,30]. This program gives VS and CS for each (crystallographically independent) node. If all nodes result equal the net is classified as uninodal, otherwise binodal, trinodal, ... \(n\)-nodal. A uninodal net is one in which all the nodes have the same VS and CS, *i.e.* are congruent. In its maximum symmetry form there is only one node in the asymmetric unit and all nodes will be related by symmetry operations (*i.e.* are equivalent). In real crystal structures, on the other hand, it is common to find low symmetry embeddings of uninodal nets (an embedding of a
graph is a realization of the graph in Euclidean space with a given geometrical description, atomic coordinates, distances and angles) where there are crystallographic distinct nodes but all have the same VS and CS, and therefore we can describe the topology of the derived net as that of an uninodal net (see Figure 1.4.6).

Then the results can be compared with a list of known nets (e.g. more than 1300 nets described in RCSR and the zeolite databases are stored in TOPOS) to find (if any) the topological type, with its given name and ideal most symmetrical structure.

**FIGURE 1.4.6**

This pair of descriptors (Vertex Symbol and Coordination Sequence for all nodes) appears to be unique for a particular net topology, i.e. they can be effectively employed to distinguish different framework types unambiguously. This statement has not been proved rigorously but long experience with databases has shown that, at present, only few theoretical different nets with the same VS and CS descriptors are known, that can still be differentiated if all the rings (not only the shortest) are computed. All these considerations belong to the context of graph theory: we can always identify two nets as isomorphic ignoring edge crossings. Two different embeddings of a net that can be deformed into each other only with edge crossings are called non-"ambient isotopic" [21,31] and therefore cannot be distinguished in graph theory. In recent years, indeed, some examples of non-"ambient isotopic" nets have been identified (see Figure 1.4.7) [3,32,33,34] for which new topological descriptors are needed, taken outside the graph theory e.g. in the context of knot theory [31].

**FIGURE 1.4.7**

Isomorphic nets can be rigorously recognized with the SYSTRE program by Delgado-Friedrichs [35], that can establish the "equilibrium" configuration of nets and assign topological unique coordinates to the vertices. By this we mean that each vertex has coordinates that are the average of the coordinates of its neighbours. Once an origin is chosen, barycentric coordinates are unique for a given choice of basis vectors. Such a placement is valuable in determining properties such as combinatorial symmetry. "Collisions" occur when two vertices have the same barycentric coordinates, but nets of such kind are still very rare in crystal chemistry (for further discussion of "collisions" see ref. 35a). Thus, for nets without collisions, SYSTRE solves the graph isomorphism problem: it unambiguously determines whether two nets have the same or different topology.
It has been suggested [5,25,36] that a limited number of "common" topologies should be sufficient to represent the large majority of organic, inorganic and metal-organic (MOFs) networks, thus furnishing a useful "network approach" to the crystal engineering of these complex systems. This important feature is true not only for single networks but also for interpenetrating 3D architectures. The distribution of the topologies found for the 482 interpenetrated structures collected in CSD and ICSD databases shows that the most common nets are by far the dia nets (ca. 42%), followed by pcu nets (ca. 18%) and by srs nets (ca. 7%) [14,15].

1.4.3.2 Tiling theory and topological approaches towards making crystals

The current growing interest for network topologies has lead to investigate in novel directions, especially for enumeration purposes, but also for crystal engineering. In the search of a rational design of coordination polymers/MOFs it appeared evident the importance of the concept of Secondary Building units (SBU) that was used for some times to describe conceptual fragments of zeolites. When polytopic units are copolymerized with metal ions, it is useful to recognize linked cluster entities in the assembled solid, each such cluster being considered a SBU. The successful design of rigid frameworks based on SBUs is the rationale for the "Scale Chemistry" [37] and the "Reticular Chemistry" [36b].

The theoretical background for the reticular synthesis arises looking at nets with a different mathematical approach, i.e. moving from the periodic graph description to the tile description of nets (based on combinatorial tiling theory) [38]. The tiles are generalized polyhedra (cages) which generate the entire structure when packed together. For each periodic net there are many possible tilings but a unique type called "natural" tiling [23a,23b,39]. The cube with eight vertices and six faces formed by four-membered rings is the natural tile of the primitive cubic net (pcu) and is symbolized as [4^6]. The adamantane unit with ten vertices is the natural tile of the diamond (dia) net. Its four faces are six-membered rings and hence the symbol is [6^4]. The natural tiling of the lonsdaleite net (lon) has equal numbers of two tiles that are [6^3] and [6^5], as shown in Figure 1.4.8. This approach classifies the nets according to the "transitivity" of the structure: if there are p kinds of vertices, q kinds of edges (links), r kinds of rings (faces of tiles) and s kinds of tiles, the transitivity is [pqrs]. The five structures srs, nbo, dia, pcu, bcu whose natural tilings have transitivity [1111] are called "regular". Their importance in reticular synthesis is comparable to that of the five platonic solids in other areas of chemistry. There is only one structure with transitivity [1112] called "quasiregular": the face-centered cubic net (fcu). The next class includes the 14
"semiregular" nets with transitivity [11rs] [23b]. All together these twenty nets are the most likely to form with one kind of SBU joined by one kind of link [40].

**FIGURE 1.4.8**

The field of infinite periodic minimal surfaces (IPMS), that was introduced few decades ago for the analysis of the topology of crystal structures [41], is a different approach to the analysis of nets: many common nets are related to the known intersection-free IPMS [42]. The IPMS studies has produced also a systematic enumeration of nets that has been recently proposed by the EPINET project (Euclidean Patterns in Non-Euclidean Tilings, see http://epinet.anu.edu.au): instead of working directly in three dimensions, the intrinsic hyperbolic geometry of IPMS is used to map 2D hyperbolic patterns into 3D Euclidean space [43].

The interested reader can find more information on the topology of networks in a recent review, with more details on what do we now know about nets [33].

**1.4.3.3 Self-catenated networks**

In the topological analysis of a network one can encounter the unusual phenomenon of self-catenaon or self-penetration. Self-catenated nets are single nets that exhibit the peculiar feature of containing rings through which pass other components of the same network. In more detail, we must refer to the topological classification of nets, represented by the Vertex Symbol, assuming that if one of the "shortest rings" is catenated by other "shortest rings" of the same net we can speak of a true case of self-catenation.

Different terms have been employed for this type of self-entangled networks. Batten and Robson [44] have underlined the relationship of these species with molecular knots (see Figure 1.4.2) but they have preferred to classify them as self-catenating or self-penetrating nets. Champness, Hubberstey, Schröder and coworkers have used the term "polyknotted coordination polymers" [45]. Also the term "intrapenetrating networks" has been employed [46]. Here we prefer to adopt the term self-catenation since the catenation happens within the net itself and there are no different nets involved. This unusual topological feature was previously observed also in simple mineral/inorganic frameworks, as in coesite (coesite), a high-pressure polymorph of silica [described as 4-connected binodal net, with Schläflı Symbol \((4^2.6^3.8)(4^2.6.8^2.9)\), recognized by O’Keeffe to be "unique among nets found in nature in that it contains 8-circuits that are linked as in a chain"
Later it was also recognized that two structures of ice, considering hydrogen bonding, are self-catenated: Ice IV (icf) and Ice XII (itv) [48].

**FIGURE 1.4.9**

Probably the first examples of 3D self-catenated frameworks within coordination polymers were described by Robson and coworkers [49]. In the species [Cd(CN)$_2$L] [L = pyrazine or 1,4-bis(4-pyridyl)butadiene] the Cd(CN)$_2$ sublattices form 4$^4$ undulated layers that are joined in a criss-cross fashion by the L spacers. Catenated hexagonal chair-like circuits are observed in the interlayer connections (see Figure 1.4.9, left). The Schlafbli Symbols of these 6-connected nets are 4$^8$.6$.8 (rob) for L = pyrazine, and 4$^4$.6$.8$ for L = 1,4-bis(4-pyridyl)butadiene, respectively, so that the requirements for self-catenation are fulfilled, since the catenated 6-rings are shortest rings [50].

Perhaps one of the most fascinating examples is represented by [Ni(tpt)(NO$_3$)$_2$] (tpt = tri-4-pyridyl-1,3,5-triazine) [51]. This contains a remarkable 3-connected chiral uniform net of 12$^3$ topology (twt VS=12$_4$.12$_7$.12$_7$) (see Figure 1.4.9, right) that was enumerated by Wells [4b] but never found previously in real species. Within uninodal 3-connected nets this is special in that it contains relatively "large" shortest rings (12-gons), the largest $n$-gons considered by Wells.

An intriguing feature of coordination network chemistry is its ability to produce rare and even only hypothetical structural motifs, given the correct building blocks. Moreover the models are reproduced on a larger scale. This is, *inter alia*, the case of [Ag(2-ethylpyrazine)$_2$(SbF$_6$)] (2-ethylpyrazine) that shows the *coe* topology [52].

Some coordination polymers exhibit notable structures containing independent polycatenated motifs (vide infra) that are joined by bridging counterions or *via* supramolecular weak interactions, thus resulting in an unique self-catenated net. A beautiful example of this class has been observed in [Cd$_2$(4,4'-pytz)$_3$(µ-NO$_3$)(NO$_3$)$_3$](MeOH) [4,4'-pytz = 3,6-bis(pyridin-4-yl)-1,2,4,5-tetrazine [45]. The structure consists of molecular ladders that give inclined catenation forming a 3D array. The ladders of the two sets are cross-linked by µ-NO$_3$ anions bridging the Cd(II) centers, resulting in the formation of a single 3D polymer, that the authors describe as a "polyknot". It should be now obvious that crossing of catenated layers (vide infra) results in a single self-catenated net [53].

1.4.4 Entangled systems

1.4.4.1 Types of entanglements
Many of the intricate organic and metal-organic networks reported in the literature are particularly intriguing because of the presence of independent motifs entangled together in different ways. After the topological classification of the individual nets we must pass to a higher level of complexity, i.e. to the analysis of the "topology of entanglements".

Entangled systems are extended arrays more complex than their constituents, that are comprised of individual motifs forming, via interlocking or interweaving, periodic architectures infinite in at least one dimension. Simple interdigitanion is not considered here. As previously stated, most of the entangled arrays can be considered regularly repeated infinite versions of finite molecular motifs like catenanes, rotaxanes and pseudo-rotaxanes.

Such molecular species are the subject of many topological investigations [9,10], especially concerning the classification of isomers within complex organic molecules [54]. Thus, in treating the complexity of entangled arrays, we will try to use concepts derived both from crystal chemistry, that has classified inorganic nets, and from the mathematical theory of knots and links. Before investigating the different structural classes we will examine some general preliminary aspects concerning the topology of entanglements.

The most common type of entanglement is represented by the numerous family of "interpenetrating networks" [2]. Interpenetration can be ascribed to the presence of large free voids in a single network, though it was shown that this phenomenon does not necessarily prevent the formation of open porous materials [55]. Wells introduced the theme of interpenetrating nets (identical or of two or more kinds) by stating that they "cannot be separated without breaking links" [4b]. Few examples were known at that time, including neptunite (2-fold interpenetrated ths), cuprite Cu$_2$O (one of the first crystal structures determined, 2-fold dia), β-quinol (H-bonded 2-fold hexagonal decorated primitive cubic peu-h 6.10$^2$), [Cu(adiponitrile)$_2$(NO$_3$)$_2$, (6-fold dia) and some others. Since then a great number of structural reports have appeared on interpenetrating nets, sustained both by coordinative or by hydrogen bonds. The most important and comprehensive contributions in the area can be found in a review by Batten and Robson [2] and in the successive highlights by Batten [48a, 56]. According to these authors interpenetrating structures, that "can be disentangled only by breaking internal connections", are characterized by the presence of infinite structurally regular motifs that must contain rings "through which independent components are inextricably entangled" [2].

However, within structures that are consistent with all the conditions described above, a distinct subclass can be recognized, namely polycatenated nets. "Polycatenanes" have the peculiar features that all the constituent motifs have lower dimensionality than that of the resulting entangled architectures and that each individual motif is catenated only with the surrounding ones but not with
all the others, like a single ring of a chain. In principle, also 0D (finite) motifs could be comprised within the possible component motifs. A comparison of the main aspects of polycatenation vs. interpenetration is given in Figure 1.4.10. In between these two classes additional intricate intermediate situations are also possible, like some recently found examples of interpenetrating 3D plus 2D [57] and 3D plus 1D frameworks [58].

FIGURE 1.4.10

In both interpenetrated and polycatenated species the individual motifs cannot be separated "without breaking rings" and, according to the concepts of chemical topology, both classes give nontrivial entanglements, in the sense that the whole arrays can be considered "topological isomers" [9,10] of their component motifs (like an n-catenane vs. the separated n rings).

At difference from the above species, other entangled systems, like polyrotaxanes, poly-pseudo-rotaxanes, interweaved chains and infinite multiple helixes, are all trivial (separable) entanglements in a strict topological sense. Polyrotaxanes deserve some comments. They are currently described as interpenetrating systems, i.e. that cannot be disentangled [2], but this relies on metrical (dimensions of the components, geometrical rigidity) or energy (barriers to dethreading) considerations rather than on topological ones. By analogy with the topological nomenclature for stereoisomers [10] we have suggested [3] to call interpenetrated and polycatenated nets "Topological" entanglements, while polyrotaxane arrays "Euclidean" entanglements (see Figure 1.4.11).

FIGURE 1.4.11

1.4.4.2 Interpenetrating networks

The "topology of interpenetration" is, at present, a still poorly explored field of chemical topology [59]. Batten and Robson [2] have treated this phenomenon through the analysis of a number of different real cases, and have introduced a currently accepted nomenclature on this subject.

The classification is based on recognizing the dimensionality (1D, 2D, 3D), the connectivity of the nodes and the topology of the individual interpenetrating motifs, the degree of interpenetration and the possible modes of interpenetration. The last point, the less known, is concerned with the relative disposition of the individual motifs in the three-dimensional space and the consequent mutual interlacing modes. It is presently difficult to answer to questions like: how many topologically distinct interpenetration modes are allowed for an n-fold diamondoid network? and also: how can we recognize when two arrays with the same degree of interpenetration and the same topology of
the individual motifs are "topologically identical" or not? We can only state that an acceptable
definition could be the following: two arrays comprised of the same number of interpenetrating
nets with the same topology can be considered "topologically identical" when distortions can be
performed that bring all the nodes to coincidence without breaking/crossing links (i.e. we could say
that, by analogy with what stated for single nets, they are "ambient isotopic" – see above).
Distinct modes of interpenetration for 2D layers [2] and dia nets [60] have been discussed.
According to the concepts introduced in Figure 1.4.10 we can have three types of interpenetrating
nets based on the dimensionality (1D, 2D and 3D).

Only one case of 1D interpenetration based on hydrogen-bonded ladder motifs has been as yet
reported [61]. On the other hand, a large variety of 2D interpenetrating networks is presently known
(with a maximum of 6-fold interpenetrated 6\(^3\) hexagonal layers [62]). 3D interpenetrating networks
are quite numerous, with interpenetration degree ranging from 2 to 18. For some times the world
records for the degree of interpenetration belonged to two diamondoid networks: within
coordination polymers to the 10-fold interpenetrated [Ag(ddn)\(_2\)](NO\(_3\)) \((\text{ddn} = 1,12-
dodecanedinitrile) [60b], while within hydrogen bonded organic supermolecules to an 11-fold
interpenetrated framework containing molecules of a tetrphenol as tetrahedral centres and
benzoquinone units as rods [63]. Only very recently Zaworotko and coworkers have described the
exceptional structure of the H-bonded net formed by trimesic acid and 1,2-bis(4-pyridyl)ethane in
the ratio 2:3, containing a 18-fold srs net [64].

The analysis and comparison of interpenetrated networks is often a difficult task and a time
expensive work because of the structural complexity of these systems and the enormous growth of
their number, that requires the use of some computer-aided procedure. A recent program suited for
this purpose is TOPOS. The automatic investigation with this package [30] has many advantages: i)
the possibility to process a large number of structural data; ii) the automatic determination of the
interpenetration degree and network relationships; iii) the automatic simplification and topological
classification. This analysis of the crystal structures has evidenced that distinct classes can be
recognized, corresponding to the different modes in which individual identical 3D motifs can
interpenetrate, that are represented by the operations generating the overall array from a single net.
The approach is strictly related to the actual crystallographic structures rather than to the "idealized"
simplified networks in their highest symmetry. Three classes are defined, independently from the
network topology (see Figure 1.4.12) [for the full details on these classes see refs. 14,15].

Class I (Translational). The individual nets are exclusively related by translations. The degree of
interpenetration \(Z\) corresponds to the translational degree of interpenetration \(Z_T\). There are two
distinct subclasses (Ia and Ib) depending on the presence or not of a full interpenetration vector. In
class Ia all the independent nets are related by a single vector and the whole interpenetrated array is generated by translating a single net \((Z_t - 1)\) times this vector. Note that many different full interpenetration vectors can exist in species belonging to this class; of them the shortest one is selected. On the other hand, in class Ib a full interpenetration vector does not exist and the whole array is generated by application of more than one translational operation. While class Ia is numerous the examples of class Ib are much rare (less than 3\% of class I).

Class II (Non-translational). The individual nets are related by means of space group symmetry elements, mainly inversion centres, but also proper rotational axes, screw axes and glide planes. The degree of interpenetration \(Z\) corresponds to the non-translational degree \(Z_n\), i.e. the order of the symmetry element that generates the interpenetrated array from the single net. In almost all cases \(Z_n\) is 2, but few examples with \(Z_n\) up to 4 are known.

The existence of compounds containing more than one interpenetration symmetry element cannot be ruled out. This require the introduction of an additional sub-classification, similar to the division of class I, i.e. class IIa with a unique full interpenetration symmetry element and class IIb with different partial interpenetration symmetry elements (only one real example is known [15]).

Class III (Translational and non-translational). The overall entanglement is generated both by pure translations and by space group symmetry elements. The value of \(Z\) is given by the product \(Z_t \times Z_n\).

**FIGURE 1.4.12**

The complete search for 3D equivalent interpenetrating networks with TOPOS in the CSD and ICSD structural databases has produced lists of 301 and 144 reference codes, respectively. It was observed that 57\% of the structures falls in class I of translational interpenetration (that favours high degrees of interpenetration), while 40\% belongs to class II (non-translational) with degree of interpenetration equal to 2 for almost all (there are only 5 known structures with degree 3 or 4). Class III is rather unusual (3\%) and presents always a degree of interpenetration of 4 or more; the highest known case of 18-fold srs interpenetration quoted above belongs to this class. It was recently proposed [65] that interpenetrating networks (called "catenated" therein) could be differentiated on the basis of the relative displacement of the subnets: so we have "interpenetration", when the frameworks are maximally displaced from each other, or "interweaving" when they are minimally displaced and exhibit many close contacts. However, a quantitative criterion to establish when the separation is maximal or minimal is still lacking, and difficult to find especially with a degree of interpenetration exceeding 2.
1.4.4.3 Polycatenated networks

The main feature of polycatenation consists in that the whole catenated array has a higher dimensionality than that of each of the component motifs. These motifs can be, in principle, 0D, 1D or 2D species that must contain closed loops and that are interlocked, as for interpenetrating nets, via topological Hopf links [31] (see Figure 1.4.11). Each motif can be catenated with a finite or also with an infinite number of other independent motifs but not with all (see Figure 1.4.10).

The classification of these entanglements can be established again by assigning in each case: i) the dimensionality and topology of the individual motifs; ii) the mode of catenation, i.e. the mutual orientation and interrelation of the component motifs, and iii) the "degree of entanglement".

The last point requires some comments. While in a $n$-fold interpenetrated networks we can easily assign the degree of interpenetration since the whole array contains a finite number of independent nets, in a polycatenated species we are forced to introduce different concepts since each individual motif can give finite or infinite interlocking with the other motifs (Figure 1.4.10). In the former case we must specify only the number $n$ of motifs effectively entangled with each motif, while in the second case, the number of rings of other motifs interlocked with a single ring of each component should be specified (and in general different values are possible for the different components).

The different types of polycatenated species can be enumerated and classified on the basis of the increasing dimensionality of the component motifs (0D, 1D or 2D)[3]. Finite (0D) motifs, containing closed circuits, can give, in principle, catenation into infinite periodic arrays (from 1D up to 3D), though no real example has been as yet characterized. Examples of polycatenated species containing many molecular rings have been described within complex organic species [54], proteins [66] and synthetic DNA assemblies [67].

Polycatenation of 1D and 2D nets can occur essentially in two modes that are described as "parallel" and "inclined", according to the nomenclature introduced by Batten and Robson [2]. Different types of 1D motifs are suitable to give polycatenation, including chains of alternating rings and rods, ribbons of rings, molecular ladders and more complex species. Some examples are illustrated in Figure 1.4.13. Almost all the known real cases are, at present, based on infinite molecular ladders interlocked to give 2D or 3D entanglements [68]. An example of catenated tubular motifs giving 2D layers has also been recently reported [69] (see Figure 1.4.13).

FIGURE 1.4.13

Interlocked 2D layers can exhibit different relative orientations of the planes of the independent motifs. When all the entangled sheets are parallel and have a common average plane the resulting
array is an \( n \)-fold interpenetrated 2D structure, with no increase in dimensionality and a finite number of interweaved motifs (see an example in Figure 1.4.14). If, otherwise, the independent layers show average planes that are parallel but displaced in a perpendicular direction, they generate a polycatenated 3D architecture. This "parallel" catenation can occur either because the sheets are undulated simple layers or because they are multiple layers, in both cases exhibiting some thickness (see Figures 1.4.14, left, and 1.4.15). Many cases are known that have been previously reviewed [3].

**FIGURE 1.4.14**

**FIGURE 1.4.15**

Polycatenation can also involve different sets of 2D sheets (usually two) that cross at a certain angle, in the mode that has been called "inclined" [2] (see Figure 1.4.14, right). The examples of this class are numerous, the majority of which consists of two identical sets of 2D parallel layers, of \( 6^3 \) or \( 4^4 \) topology, spanning two different stacking directions. In these species there is an increase of dimensionality (2D \( \rightarrow \) 3D) and each individual layer is catenated with an infinite number of other inclined layers but, obviously, not with all the frames contained in the 3D array. Moreover, in the analysis of these species different modes of interlocking of the two independent sets have been envisaged for both topologies [2]. For \( 4^4 \) layers three possible arrangements have been suggested by Zaworotko and coworkers [70], called parallel-parallel (p-p), parallel-diagonal (p-d) and diagonal-diagonal (d-d), depending on how the networks orient and penetrate through each other (see some examples in Figure 1.4.16). Systematic enumerations of these entangled species have already appeared in some reviews [2,44,48a,56,70].

**FIGURE 1.4.16**

Only in few cases major variations of the above inclined polycatenation scheme were observed. For instance, catenation can involve two sets of 2D layers of different topology, as in 

\[
[\text{Ni}(\text{azpy})_2(\text{NO}_3)_2][\text{Ni}_2(\text{azpy})_3(\text{NO}_3)_4].4\text{CH}_2\text{Cl}_2 \quad \text{azpy} = \text{trans-4,4'}-\text{azobis(pyridine)}]
\]

containing both \( 6^3 \) and \( 4^4 \) layers [71]. Another variation is represented by the presence of more than two distinct sets of layers. No real case was known in 1998 when Batten and Robson [2] had suggested the possibility of finding three different mutually perpendicular stacks; since then few examples have been discovered and one is illustrated in Figure 1.4.16 (left), namely

\[
[\text{Ni}_6(\text{bpe})_{10}(\text{H}_2\text{O})]_6(\text{SO}_4)\text{H}_2\text{O} \quad \text{bpe = 1,2-bis(4-pyridyl)ethane}]
\]

that contains three distinct...
sets of $4^4$ layers spanning three different spatial orientations and giving inclined mutual penetration.

Polycatenation involving motifs of different dimensionality is also known, though quite rare, as in $[\text{Cu}_5(\text{bpp})_8(\text{SO}_4)_4(\text{EtOH})(\text{H}_2\text{O})_3](\text{SO}_4)\text{EtOH}.25.5\text{H}_2\text{O}$ \[ \text{bpp} = 1,3\text{-bis(4-pyridyl)propane} \] containing two different polymeric motifs entangled to give an unique 3D array: ribbons of rings and two-dimensional tessellated sheets of $4^4$ topology (Figure 1.4.16, right).

### 1.4.4.4 Borromean networks

Molecular motifs containing different rings could give inextricable entanglements not only via Hopf links. An alternative way involving at least three closed circuits at a time is represented by the Borromean link [3,32] (see Figure 1.4.11). This is a nontrivial link in which three rings are entangled in such a way that any two component rings form a trivial link, \textit{i.e.} if any one ring is cut the other two are free to separate. Chemists for a long time have considered the realization of a molecular Borromean link a synthetic goal of great interest; an example has been very recently reported by Stoddart and coworkers, comprised of three macrocyclic Borromean rings obtained by metal templated synthesis [74]. Previously, only one species was known, constructed from single-stranded DNA by Seeman and coworkers in 1997 [75]. Using Borromean links, however, infinite 1D, 2D or 3D arrays could be imagined. Links like these could appear only mathematical curiosities; indeed they have been identified in some real examples of infinite interlocked nets. Borromean links are present in two types of arrays: (2D $\rightarrow$ 2D) entanglements of three layers and (2D $\rightarrow$ 3D) entanglements of infinite layers [32]. Three cases of Borromean 3-fold entangled 2D layers have been recognized, all exhibiting a $6^3$ layer topology [32,76] (see Figure 1.4.11, upper right; one can easily realize that the black net is completely located above the grey one, the grey net above the white one, but the grey net lies above the white one).

**FIGURE 1.4.17**

A Borromean (2D $\rightarrow$ 3D) entanglement can be envisaged in the structures of two isomorphous polymeric silver(I) complexes reported by Chen and coworkers, $[\text{Ag}_2(\text{H}_2\text{L})_3](\text{NO}_3)_2$ and $[\text{Ag}_2(\text{H}_2\text{L})_3](\text{ClO}_4)_2$ \[ \text{H}_2\text{L} = \text{N,N'-bis(salicylidene)-1,4-di-aminobutane} \] [77] and in another silver species with a similar formula [78]. They are comprised of highly undulated $6^3$ layers of 3-connected silver centres (Figure 1.4.17). The silver atoms exhibit interlayer unsupported $\text{Ag} \cdots \text{Ag}$ interactions and, taking into account these contacts, a single 4-connected 3D array results, that can be described as self-catenated embedding of \textit{dia} (regular \textit{dia} - see \textit{e.g.} Figures 1.4.5, 1.4.7 and 1.4.8
- and self-dia are non-"ambient isotopic" and have obviously the same Schlӓfli Symbol, Vertex Symbol, as well as the Coordination Sequence, but dia cannot be deformed into self-dia without edge crossings) [32,34]. On the other hand, and much more interestingly, if the Ag⋯Ag interactions are neglected, the layers are not (2D → 3D) polycatenated but are interlinked via Borromean links involving three layers at a time. The whole array represents the first infinite case of n-Borromean links (Figure 1.4.17).

1.4.4.5 Other entanglements

Other known types of infinite entanglements are comprised of finite or infinite components that can be "ideally" separated without breaking effective topological links. We are speaking of polythreaded arrays, i.e. extended periodic analogues of molecular rotaxanes and pseudo-rotaxanes. The term "Euclidean entanglements" was suggested for polyrotaxanes, meaning that only the presence of geometrical or energetical (non topological) constrains can prevent the separation of the individual motifs [79]. On the other hand, poly-pseudo-rotaxanes contain motifs that are threaded by chains or strings which, in principle, can be slipped off; they display a type of entanglement that is neither topological nor Euclidean.

Polythreaded systems contain motifs that are interweaved via rotaxane-like mechanical links and this implies the presence of closed loops as well as of elements that can thread the loops (Figure 1.4.2). These two types of moieties may belong to the same unit or may be separately supplied by motifs having different structures. The constituent motifs could be, in principle, 0D species, 1D polymers or arrays of higher dimensionality. The resulting array can show the same or an increased dimensionality with respect to that of the polythreaded units.

Known examples involving 0D motifs, i.e. molecular "beads" (cucurbituril molecules), threaded by coordination polymers of different topology have been described by Kim and coworkers [80]. Many examples of extended systems that "cannot be disentangled" have been reported very recently. The 1D chain motif comprised of alternating rings and rods is particularly suitable for polythreading since it contains both the elements needed in a rotaxane-like mechanical linkage. Chains of this type have been found to give (1D → 1D) [81], (1D → 2D) parallel [82] (see Figure 1.4.18, a and b) and inclined [82, 83] (see Figure 1.4.11, bottom right) polythreaded arrays.

FIGURE 1.4.18
Numerous entangled arrays containing "separable" motifs (poly-
pseudo-rotaxanes), like those shown in Figure 1.4.18 (right) have also been reported [see ref. 3].

Architectures of interweaved 1D motifs display different types of entanglements that are neither topological nor Euclidean. Polymeric chains, both rigid or flexible, represent the most simple and common structural extended motif. The packing of 1D polymers usually occurs with parallel orientation of all the chains; less commonly they can span two different directions on alternate layers. Independent chains can be sometimes connected into pairs or into extended 2D or 3D arrays by weak supramolecular interactions. Quite rare are, on the other hand, other types of associations of the chains resulting in entangled systems of unusual topologies, including chains woven like warp-and-woof threads in a cloth to give 2D sheets (Figure 1.4.19, left) and infinite multiple helixes (Figure 1.4.19, right).

FIGURE 1.4.19

1.4.5. Conclusions
We have attempted to rationalize here the structures of extended frames at different levels of complexity in terms of the network topology. With the aim to establish useful relationships between structures and properties [84] a careful analysis of the topology is unavoidable, particularly for the complicated species that are more and more discovered. Indeed, phenomena like interpenetration are not only structural curiosities, with some esthetical appeal, but can play an effective role on the control of the properties of materials, as shown, inter alia, by their influence on network porosity [55a,65a] and by their capability to produce anomalous magnetic properties [85].
A similar problem is encountered in the construction of the graph of a molecule for the study of its topology. While the identification of the vertex set is straightforward, the relationship of the edges in the graph to the bonds in the molecule is less well defined, and we should establish which bonds in the molecule can be regarded as "topologically significant". According to Mislow, a considerable arbitrariness is inevitably implicit in any graph, and "whether or not a given geometrically chiral molecular model is considered to be also topologically chiral depends on which subset of bonds in the molecule is considered to be topologically significant" [9]. Following the common usage in organic chemistry, Walba suggested to consider topologically significant only covalent bonds [10], but there is no obvious reason to limit the "edge set" to these bonds, thus ignoring the whole area of supramolecular chemistry.

[20] For enumeration and computational purposes, the infinite graph (i.e. our net) is reduced to a finite "labelled quotient graphs", closely related to a crystallographic primitive unit cell, where the labelled edges in the quotient graph describe the connectivity of the nodes. For a given number of nodes per unit cell all labelled quotient graphs which have a predefined connectivity can be found in: S. J. Chung, Th. Hahn, W. E. Klee, Acta Crystallogr. 1984, A40, 42; W. E. Klee, Cryst. Res. Technol. 2004, 39, 959; J.-G. Eon, Acta Crystallogr. 2005, A61, 501; ref. 21. This approach has been applied, for instance, for the search of novel carbon polymorphs, see: G. Thimm, Z.

[22] This nomenclature includes some simply related nets as the augmented net and the edge net called \textit{xxx-a} and \textit{xxx-e} respectively. An \textit{augmented net} is one in which the vertices of the original net are replaced by a polygon or polyhedron corresponding to the original coordination figure. The \textit{edge net} (also expanded net) is obtained from the original net by placing vertices in the middle of the edges, discarding the original vertices and edges, and joining the new vertices to enclose the coordination figure of the original vertices. Moreover \textit{decorated nets} (\textit{xxx-f}, \textit{g} etc.) are obtained by replacing the vertices of the original net by groups of vertices. Augmented nets are special cases of decorated nets. See RCSR web page and ref. 23.


[26] In a more rigorous graph-theoretical approach we should use the term \textit{n}-coordinated instead of \textit{n}-connected, but we keep here the word \textit{connected} to indicated what is clear to chemists: for example, a metal could be 6-coordinated but give only a 3-connected net if three coordination sites are occupied by ligands that are not links of the network.


[28] An equivalent definition for \textit{ring} is an \textit{n}-membered circuit that represents the shortest possible path connecting \textit{all} the \([n(n-1)/2]\) pairs of nodes belonging to that circuit.


[30] The program package TOPOS 4.0 with an advanced graphical interface (available at http://www.topos.ssu.samara.ru) was recently improved for the automatic determination and classification of the interpenetration degree, see refs. 14 and 15. The program is also able to analyze and simplify complex groups (including H-bonded networks) and to assign the topology of the resulting network according to the RCSR proposed symbol. As a result, typical crystal structure of organic, inorganic, or coordination compound may be processed in a few minutes from the .res or .cif files, to get a comprehensive description of the topology and of the interpenetration (if any). A detailed analysis of Voronoi-Dirichlet partition of crystal space and estimation of related crystallochemical parameters are also available in TOPOS. See, V.A. Blatov, \textit{Cryst. Rev.} 2004, 10, 249.


[48] (a) S.R Batten, *CrystEngComm*. 2001, 3, 67; (b) M. O’Keeffe, *Nature* 1998, 392, 879. However, taking into account our definition of self-catenation, for ifc the catenated six and ten membered circuits are not both "shortest rings"; and for itv the catenated 8-rings are not "strong rings". It follows that a more detailed classification is possible considering also not only the "shortest rings" defining the VS but also larger ring that may exists (as for ifc), and the "strong rings" (as for itv) [see ref. 21 for definition of all kind of rings].


[53] Self-catenation is not observed only in 3D nets but is possible also in 2D nets: few rare examples are known [see ref. 3] and two recent are: the 4-connected layers in a Cd coordination polymer (G. O. Lloyd, J. L. Atwood, L. J. Barbour, *Chem. Commun.* 2005, 1845 and the 6-connected layers in a supramolecular arrangement of a tetrazole derivative (A. T. Rizk, C.A. Kilner, M.A. Halcerow *CrystEngComm*, 2005, 7, 359.


[59] Two-fold interpenetration in some prototypical nets has been discussed in terms of dual of the tiling of the net by O’Keeffe and coworkers (see ref. 39a). The dual of a tiling is obtained by putting new vertices in the center of the tiles and connecting such vertices by edges passing through common faces (each face of a tiling is common to two tiles) forming an interpenetrating net, so that all rings (faces) of the original structure are linked (catenated) to faces of the dual one and vice versa. When the tiling of the net and its dual are the same, we speak of self-dual nets (e.g. dia, pcu, srs, fcu, eds).


[79] Not only poly-pseudo-rotaxanes but also polyrotaxanes should be considered trivial topological entanglements, extending the concepts developed for the related molecular entities. By
means of "ideal" continuous deformations we could separate the components of any finite portion of a polyrotaxane. However, the extended motifs under examination can be considered infinite entities. Including this additional "boundary condition" a different topological description could result for such interweaving systems, but this is at present an almost completely unexplored area of chemical topology.

Figure Captions

**Figure 1.4.1.** An alternative selection of nodes gives two distinct topological descriptions, here illustrated for the 2-fold interpenetrated H-bonded structure of H$_2$Te$_2$O$_3$F$_4$ [J. C. Jumas, M. Maurin, E. Philippot, *J. Fluor. Chem.*, 1976, 8, 329]: 3-connected ThSi$_2$ (ths) with Te, and diamond (dia) with the molecule centroid.

**Figure 1.4.2.** Models of links and knots for finite entities.

**Figure 1.4.3.** Nets with common topologies and their nomenclature (see text). The symbols are related to prototypical structures or lattices as follows: SrSi$_2$ (srs), NbO (nbo), primitive cubic (pcu), body centered cubic (bcu), face centered cubic (fcu), sodalite (sod), ThSi$_2$ (ths), CdSO$_4$ (cds), quartz (qtz), SrAl$_2$ (sra), PtS (pts), rutile (rtl).

**Figure 1.4.4.** In the 3-connected uninodal net rhr-a the vertex 1 with the three edges $a,b,c$ has Vertex Symbol 4.8.12 (angles $ac$: 4-ring, $ab$: 8-ring, $bc$: 12-ring, with single multiplicity for all three rings: 4,8,12). If we consider the shortest circuits we get the Schlafli Symbol 4.8.10: in fact, the angle $bc$ is included in the circuit with 10 edges [1,2,3,4,5,6,7,8,9,10] that is not a ring because is the sum of two shortest rings (there is a short-cut represented by edge $a$).

**Figure 1.4.5.** The structures of diamond (dia) (left) and lonsdaleite (hexagonal diamond) (lon) (right). The two nets have the same Schlafli and Vertex Symbol VS (top), but different Coordination Sequence (CS). The rings multiplicity for one selected angle is evidenced in grey; in both nets for each angle there are two 6-rings, in dia both have the same chair conformation, in lon the conformation is different, one chair and one boat.

**Figure 1.4.6.** The highly distorted diamondoid net observed in the 2-fold interpenetrated structure of SbCl$_3$($p$-diacetylbenzene) with a diamondoid cage in black [W. A. Baker, D. E. Williams, *Acta Crystallogr.*, 1978, B34, 1111] (left). The observed diamondoid cage (center) is compared with the undistorted adamantane cage as in diamond (right).

**Figure 1.4.7.** Two different layered nets (2-periodic) characterized by the same VS and CS that are not ambient isotopic. We cannot transform one into the other without bond/edge crossing. The layer on the left is rather common while that on the right is observed only in [Ag$_2$L$_2$(μ-PO$_2$F$_2$)](PF$_6$) [L = 1-(isocyanidomethyl)-1H-benzotriazole] [I. Ino, J.C. Zhong, M. Munakata, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga, Y. Kitamori, *Inorg. Chem.* 2000, 39, 4273].

**Figure 1.4.8.** The structures of diamond (dia) (left) and lonsdaleite (hexagonal diamond, lon) (right) showing in grey the natural tile with 10 vertices for dia (adamantane cage) with transitivity [1111] and the two natural tiles with 8 and 12 vertices for lon with transitivity [1222].

**Figure 1.4.9.** Three examples of self-catenated nets with two catenated rings (Hopf links) in black: 6-rings (rob), 8-rings (coe), 12-rings (twt).

**Figure 1.4.10.** The differences of interpenetration vs. polycatenation.

**Figure 1.4.11.** The overall view of the entanglement phenomena in extended compounds (coordination and H-bonded).

**Figure 1.4.12.** The different classes of interpenetration (translational and non-translational) illustrated with an example of 3-connected 2-fold ths.
Figure 1.4.13. Polycatenation of 1D motifs: 2D entangled layers from parallel catenation of undulating ladders (laterally catenated by two other ladders by each side) (left), and of nanotube motifs (center); 3D superstructure from catenation of ladders running in different directions (right).

Figure 1.4.14. Three possible topological entanglements of hexagonal $6^3$ layers showing the interpenetration versus catenation (parallel and inclined).

Figure 1.4.15. The 3D entanglement of parallely catenated double layers (left) and an intricate case of parallel catenation of undulated 2-fold $6^3$ layers (right) [S. Banfi, L. Carlucci, E. Caruso, G. Ciani, and D.M. Proserpio, Cryst. Growth Des. 2004, 4, 29]

Figure 1.4.16. The 3D entanglements of different inclined catenations: three sets of 2D ($4^4$) layers(left), perpendicular catenation of 2-fold $4^4$ layers (center) [K.A. Hirsch, S.R. Wilson, J.S. Moore, Chem. Commun. 1998, 13], $4^4$ layers catenated by perpendicular 1D ribbons of rings (right).

Figure 1.4.17. A Borromean (2D $\rightarrow$ 3D) entanglement of undulated ($6^3$) layers (left and center, see refs. 32,77,78). On the right is illustrated the related self-dia net discussed in the text (see also refs. 32,34).

Figure 1.4.18. Examples of polyrotaxanes and poly-pseudo-rotaxanes.

Figure 1.4.1. An alternative selection of nodes gives two distinct topological descriptions, here illustrated for the 2-fold interpenetrated H-bonded structure of \( \text{H}_2\text{Te}_2\text{O}_3\text{F}_4 \) [J. C. Jumas, M. Maurin, E. Philippot, *J. Fluor. Chem.*, 1976, 8, 329]: 3-connected \( \alpha\)-ThSi\(_2\) (ths) with Te, and diamond (dia) with the molecule centroid.

Figure 1.4.2. Models of links and knots for finite entities.

Figure 1.4.3. Nets with common topologies and their nomenclature (see text). The symbols are related to prototypical structures or lattices as follows: SrSi\(_2\) (srs), NbO (nbo), primitive cubic (pcu), body centered cubic (bcu), face centered cubic (fcu), sodalite (sod), ThSi\(_2\) (ths), CdSO\(_4\) (cds), quartz (qtz), SrAl\(_2\) (sra), PtS (pts), rutile (rtl).
In the 3-connected uninodal net rhr-a the vertex 1 with the three edges $a,b,c$ has Vertex Symbol 4.8.12 (angles $ac$: 4-ring, $ab$: 8-ring, $bc$: 12-ring, with single multiplicity for all three rings: $4,8,12$). If we consider the shortest circuits we get the Schläfli Symbol 4.8.10: in fact, the angle $bc$ is included in the circuit with 10 edges $[1,2,3,4,5,6,7,8,9,10]$ that is not a ring because is the sum of two shortest rings (there is a short-cut represented by edge $a$).

The two nets have the same Schläfli and vertex symbol VS (top), but different coordination sequence (CS). The rings multiplicity for one selected angle is evidenced in grey; in both nets for each angle there are two 6-rings, in dia both have the same chair conformation, in lon the conformation is different, one chair and one boat.

The highly distorted diamondoid net observed in the 2-fold interpenetrated structure of SbCl$_3$(p-diacetylbenezene) with a diamondoid cage in black [W. A. Baker, D. E. Williams, *Acta Crystallogr. Sect. B*, 1978, 34, 1111] (left). The observed diamondoid cage (center) is compared with the undistorted adamantane cage as in diamond (right).
Figure 1.4.7. Two different layered nets (2-periodic) characterized by the same VS and CS that are not ambient isotopic. We cannot transform one into the other without bond/edge crossing. The layer on the left is rather common while that on the right is observed only in $[\text{Ag}_2\text{L}_2(\mu-\text{PO}_2\text{F}_2)](\text{PF}_6)$ [L = 1-(isocyanidomethyl)-1H-benzotriazole] [I. Ino, J.C. Zhong, M. Munakata, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga, Y. Kitamori, Inorg. Chem. 2000, 39, 4273].

Figure 1.4.8. The structures of diamond (dia) (left) and lonsdaleite (hexagonal diamond, lon) (right) showing in grey the natural tile with 10 vertices for dia (adamantane cage) with transitivity [1111] and the two natural tiles with 8 and 12 vertices for lon with transitivity [1222].

Figure 1.4.9. Three examples of self-catenated nets with two catenated rings (Hopf links) in black: 6-rings (rob), 8-rings (coe), 12-rings (twt).

Figure 1.4.10. The differences of interpenetration vs. polycatenation.
Figure 1.4.11. The overall view of the entanglement phenomena in extended compounds (coordination and H-bonded).

Figure 1.4.12. The different classes of interpenetration (translational and non-translational) illustrated with an example of 3-connected 2-fold ths.

Figure 1.4.13. Polycatenation of 1D motifs: 2D entangled layers from parallel catenation of undulating ladders (laterally catenated by two other ladders by each side) (left), and of nanotube motifs (center); 3D superstructure from catenation of ladders running in different directions (right).

Figure 1.4.14. Three possible topological entanglements of hexagonal $6^3$ layers showing the interpenetration versus catenation (parallel and inclined).
Figure 1.4.15. The 3D entanglement of parallely catenated double layers (left) and an intricate case of parallel catenation of undulated 2-fold 6^3 layers (right) [S. Banfi, L. Carlucci, E. Caruso, G. Ciani, D.M. Proserpio, *Cryst. Growth Des.* 2004, 4, 29]

Figure 1.4.16. The 3D entanglements of different inclined catenations: three sets of 2D 4^3 layers (left), perpendicular catenation of 2-fold 4^4 layers (center) [K.A. Hirsch, S.R. Wilson, J.S. Moore, *Chem. Commun.* 1998, 13], 4^4 layers catenated by perpendicular 1D ribbons of rings (right).

Figure 1.4.17. A Borromean (2D → 3D) entanglement of undulated 6^3 layers (left and center, see refs. 32,77,78). On the right is illustrated the related self-dia net discussed in the text (see also refs. 32,34).

Figure 1.4.18. Examples of polyrotanes and polypseudo-rotaxanes.