

Building Units Design and Scale Chemistry

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DEDICATED TO MIKE O'KEEFFE AND TO THE MEMORY OF LINUS PAULING

The concept of a building unit (BU) is used in two ways: the first is an *a posteriori* tool for description of structures which can be used to *imagine* new topologies originating from the description; the second one, restricted to the routes leading to the solid from the solution, starts from the *reality* of these building units in the solution to design new solids obtained by the tuned precipitation of these BUs with proper counterions. The room temperature and the hydrothermal routes are examined. The existence of BUs with different sizes with close topologies, revealed by numerous examples, leads us to define the notion of "scale chemistry" which concerns the edification of solids with various BUs, either organic, hybrid, or inorganic, and the consequences it has for the corresponding frameworks and the voids they generate. Not only the framework is important, and applications of the existence of large cavities are discussed. The paper ends with a discussion of the new trends which arise from this topological concept.   2000 Academic Press

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1. "IL N'Y A QU'UNE CHIMIE" (J. MARIE LEHN)

Indeed, at the end of the 20th century, chemical sciences are at a key moment, a " χ Xing", and the usual frontiers between organic and inorganic chemistry, which had their fans, are progressively vanishing to give rise to a more general approach, including both sides, their specificities but also their common points. The improvements of crystallographic techniques, and the development of crystal chemistry and of structural representations, greatly helped toward this merging. The concept of structural physicochemistry, starting from synthesis toward the examination of the final geometry of the assemblies, whatever their nature, and the explanation of their properties, progressively took a major place in the publications. The assimilation of chemists to architects of matter has never been so powerful as in the 1990s. Indeed, there is only one chemistry, with different objects and different kinds of bondings (ionic, covalent, hydrogen, van der Waals, ...), and the talent of modern chemists is needed to combine them in

a topological approach, associating inorganic and organic moieties, the contrast of their bondings, for creating new extraordinary solids with additive properties. This chemical topography, which has been possible—and one must repeat this—owing to the developments of crystallographic techniques, is based on the concept of building units (hereafter denoted BU). This concept originates from thousands and thousands of structure determinations, followed by the examination of their common features and the reflections of some very few scientists on this point. We shall show the ways this concept opens: structural descriptions, design of new solids from the solution, size and topology of the BUs, and its consequence, hereafter called "scale chemistry," its incidence both on the vacancies in the solid and their use for chemical purposes and the ability for simulating such structures.

2. BUILDING UNITS: WHAT DOES IT MEAN?

It is at the beginning a *topographic notion*. One can define the BU as the minimum assembly of atoms, ions, or molecules which, by condensation of the group with others (identical or different), gives rise to the final solid, whatever the symmetry and/or the dimensionality. The BUs act as "bricks" for the edification of the structures and their size can be completely different with the considered solid, like in architecture: bricks of a few tens of centimeters can build a Renaissance castle as well as stones of several meters can create the Pyramids, or marble stones and pillars the Pisa tower (Fig. 1).

Pauling (1) was at the origin of the concept of BU, when he defined the coordination polyhedra for the description of structures, and stated the Pauling's rules. For instance, in the ReO_3 structure (Fig. 2), the BU is the octahedron, the condensation of which by vertices leading to the three-dimensional solid. It is important to distinguish between the notions of BU and of asymmetric units; the latter refer to crystallographic sites and therefore to symmetry whereas the former, in an ionic approach, are associated with anionic coordination of one or several cations defining the metallic

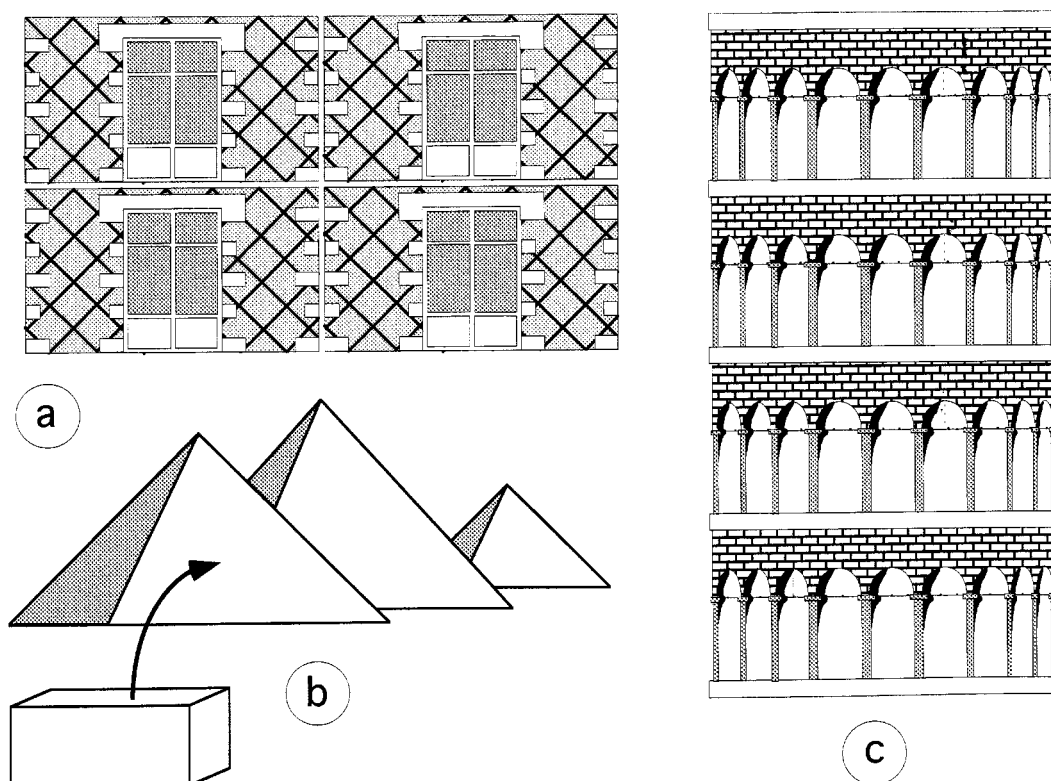


FIG. 1. Different bricks used in Amboise (France) for the Renaissance castle (a), in Gizeh for the Pyramids (b), and in the (idealized and vertical!) Pisa Tower.

centers of the BUs. Further, the concept of BU was particularly developed by Meier and Olson (2) for the description of zeolitic structures.

This general definition applies to all sorts of chemistry and therefore to all types of chemical bonding: organic chemistry, where the BUs are the molecules themselves; organometallic chemistry, where the BU consists of the organically chelated metallic centers; and solid-state chemistry, where the association of polyhedra generates the building block. It is also worth noting that the idea of BUs initially implies thermodynamically stable states, the final compound representing the ultimate step of the formation of the solid, whatever the mechanism of formation, and this

is a key point. This is why the BU concept was originally just a tool for the description of structures.

2.1. Building Units: an a Posteriori Tool for an Easy Description and Chemical Imagination

This approach was and is always based on a *molecular* description. Emphasis is put on the BU, not on the solid itself. We shall see below the danger of such an approach. Indeed, and even if it was not historically the case, what is important is the genesis of the solid, and not the BU. That means that the concept of the BU cannot be dissociated from the notion of assembly of the BU, i.e., the solid itself. However, for obvious historical disciplinary reasons, and even now, it is often the BU which is described in the litterature, and not the assembly. Solid-state organic chemists publish the structure of their molecules but do not mention how they are organized in the solid. Ten years ago, inorganic chemists described the beautiful and sometimes extraordinary molecular moieties of the solids they isolated (Figs. 3a–3c) because their science was in essence molecular.

They focused on the brick, not on the house. Solid-state chemists, in contrast, because their chemistry was essentially two- or three-dimensional, started from the framework to

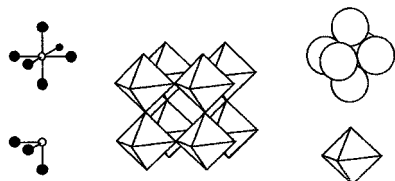


FIG. 2. Polyhedral representation of the ReO_3 structure with balls and sticks, space-filling and polyhedral representations of the BU. On the left is the asymmetric unit with one Re and three oxygens.

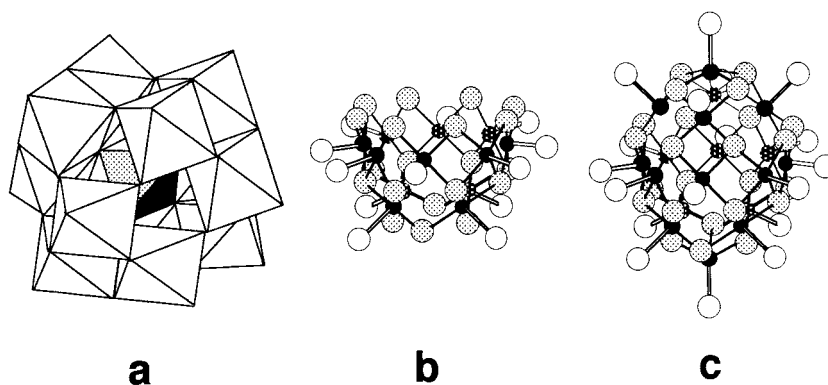


FIG. 3. BU representation of the structures of (a) the Keggin ion (from (3)), (b) the $[V_{12}O_{32}]^{4-}$ basket in $(PPh_4)_4 [(MeCN)(V_{12}O_{32})]$ from (4), and (c) the $[V_{18}O_{42}]^{4-}$ sphere in $K_9[H_4(V_{18}O_{42})(Cl)]$ from (5).

divide it in BUs which, by translation operations, regenerated the solid (Fig. 4). These two different approaches converge now as it will be seen below.

The description of structures from BUs has, however, some advantages. First, within a chemical family, it allows us to identify the very few BUs which are able to describe the whole family. A nice example was recently provided by Raveau's group on molybdenum phosphates (8). The structures of the $M-O-P$ family, which contains more than 50 members, are built up from only seven n -meric BUs ($n = 2-4$) whose connections lead to the frameworks (Fig. 5). The same approach led us to describe all the structures of 3d transition metal fluorides from only five building units (9).

The second advantage concerns the comparison of structures which exhibit the same BU but with different topologies. The examination of the latter rationalizes the organization of the known structures and allows for the

search of new topologies based on these BUs. A recent example concerns the ULM and MIL families (10). These families of solids with an open framework are fluorinated gallophosphates templated with various amines, obtained by hydrothermal synthesis. Most of them are built from a hexameric unit (called SBU-6 in our papers) containing three phosphate groups and three gallium polyhedra (one octahedron and two trigonal bipyramids) (Fig. 6).

According to the nature of the templating amine, different structures are obtained, all exhibiting the hexamer. The different types of trans corner linkage of the BUs give rise to linear or zig-zag chains (Fig. 6). The connections of the latter by translation and/or by a mirror plane operation lead to the known structures. Starting from that, a topological

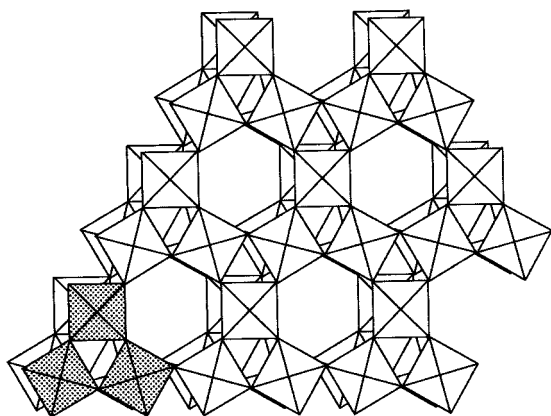


FIG. 4. Description of the HTB- FeF_3 structure in terms of trimeric BUs (from (7)). By translation, the trimeric unit of corner-shared octahedra regenerates the whole solid.

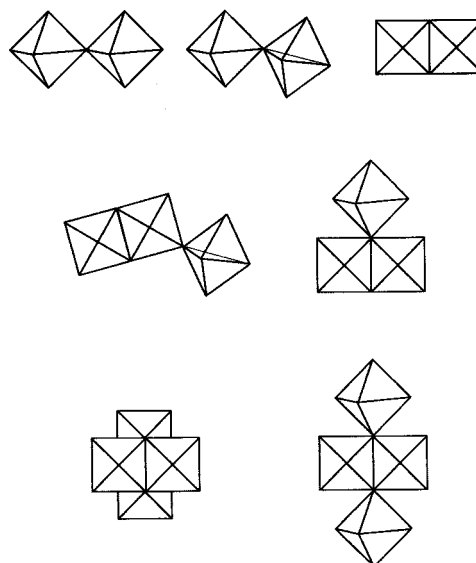


FIG. 5. Different BUs which describe all the $M-O-P$ structural chemistry (from (8)).

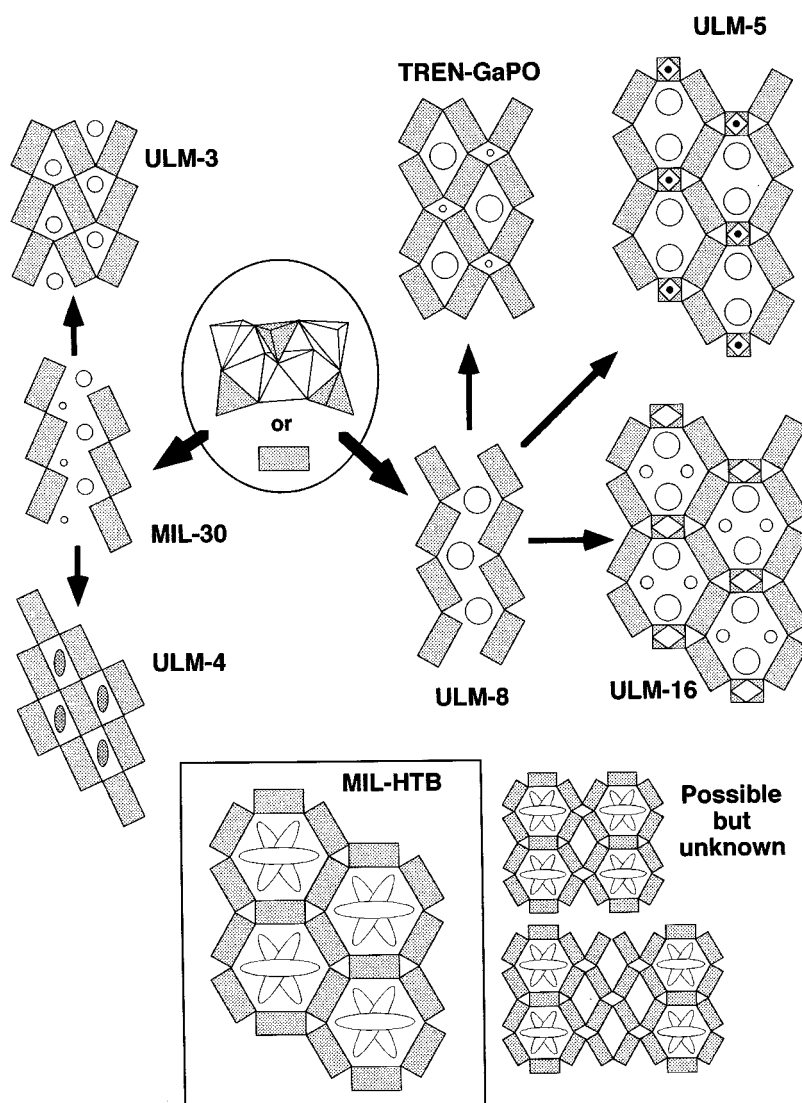


FIG. 6. Some of the topologies built from the hexameric unit $\text{Ga}_3(\text{PO}_4)_3\text{F}_2$ (within the circle, and represented after by a shaded rectangle) in the ULM and MIL-*n* families. The topology of MIL-HTB (insert, bottom) was expected before finding the conditions for obtaining it. The various amines (see Ref. 10) are represented by circles or ellipses. On the bottom right, some possible but unknown structures are presented.

reflection allows us to imagine new and unknown arrangements of these hexamers, and to try to synthesize the corresponding compounds. This was just done for MIL-HTB. Indeed, in our porous solids, we had no example of hexagonal tunnels with only SBU-6. In ULM-5 and -16, the chains of hexamers were linked by either octameric tetrahedral units (ULM-5) or infinite double crankshaft chains. By an appropriate choice of the geometry of template, we found the right conditions of pH and concentration to obtain the desired compound (11). Such a reflection from the BU to its possible arrangement in the solid will probably be developed as a tool in the future. Indeed, there is no limitation to the imagination in topology. For

instance, Fig. 6 shows (bottom right) some topologies based on the connection of exclusively SBU-6, using intergrowth of known arrangements. The corresponding solids are not yet discovered, but why not?

This approach has also an advantage: it requires that we take into account not only the BU, which has very often a formal charge different of zero, but also the counterion whose role, despite essential, is frequently neglected. The edification of the solid requires the interaction between them. We need bricks, but also cement to build the house! Now, in the structural papers of molecular chemists, we see more and more the whole structure described and not only the BU.

The charge and the shape of the counterion largely influence the nature and the structure of the final solid. Solid-state chemists know that very well. As soon as a new structure type containing occluded cations (frequently alkaline or alkaline-earth ions) is discovered, the first thing to do is to change the nature of the inserted cation in order to see the influence of its size on the stability of the structure type. The size of the cation is important, but so is its charge. Changing the charge of the counterion has immediately an effect on the charge of the BU, and if chemistry does not take into account a correlative change of the metal within the BU, it is clear that the structure will change. A lot of work has been done using this idea because, keeping the same structure type, an intelligent substitution can provide the appearance of a property. The famous—and trivial—example of the perovskite structure illustrates that. The substitution of Ba^{2+} by K^+ , comparable in size, in BaTi(IV)O_3 requires that titanium(IV) be replaced by Nb(V) in order to keep the same structure for KNbO_3 . If Li^+ is used, it is too small to stay in the cuboctahedral cavity of the perovskite, and the structure of LiNbO_3 does not belong to the perovskite family. Moreover, the substitution can affect also the anionic part of the network, and if size criteria are respected, the structure remains unchanged. For instance, KMn(II)F_3 is also a perovskite, and this time, the substitution in an invariant structure provides another physical property, here the magnetism.

Finally, and many chemists use it in this way, the BU concept is a useful *a posteriori* tool to describe, analyze, and imagine within a certain type of chemistry. The numerous known structures can all be described from BUs which are always polyhedral clusters. A large number of them are described by M. O’Keeffe and B. G. Hyde in (12). The future of this approach is essentially to imagine new nets of BUs, following the way that A. F. Wells (13), W. M. Meier (14), J. V. Smith (15), M. O’Keeffe (16), and more recently M. M. J. Treacy (17) and O. Delgado Friedrichs (18) opened, and, of course, accordingly, carry out a creative chemistry. This is another key point. Indeed, in this approach, the chemist has no mastery on the BU. He observes it, he plays with it, but he is unable to create it. However, the BU exists. The challenge is therefore to build it at the very beginning of the reaction, to be sure that it is a stable entity, and to imagine ways of connection of these BUs for the final solid.

2.2. Building Units: a Challenge for Creativity and Design

It is clear that such a challenge can be fulfilled only when chemistry occurs in the solution. “All-solid” chemistry, which implies only diffusion processes, cannot be concerned by this challenge. All the reactions and all the design will occur in an heterogeneous medium, made by the solvent, the soluble species it contains, the solids, intermediary or thermodynamically stable, and the exchanges between them. That

means a very complex physical chemistry of the solutions on which, and owing to the existence of numerous spectroscopies, scientists fortunately have a good knowledge as long as reactions occur around room temperature (19).

The problem is much more difficult when hydrothermal conditions are required, because almost nothing is known for these conditions. Indeed, the properties of the solvent drastically change (dielectric constant, polarizing power, ...) and affect the nature of the species in the solution. Simultaneously, the use of hydrothermal medium in the synthesis has dramatically increased during the past 10 years because of its richness for the discovery of new phases, sometimes in contradiction with set ideas (for instance, despite the common belief concerning the sensitivity of fluorides toward hydrolysis, we showed that, under hydrothermal conditions (20), fluorinated species are stable in aqueous solutions and lead to purely fluorinated solids, even at temperatures as high as 450°C). This section will therefore dissociate the two situations.

Room temperature reactions. Under these conditions, knowledge about the chemistry of the solutions has identified the species and their stability *vs* chemical conditions. In most of the cases, the moiety which exists in the solution will be found in the final solid. Therefore, the science consists of finding good conditions and good reactants for precipitating the desired solid. For that, chemists will play on the contrast of bonding interactions to create the design of the solid compound.

In organic solid-state chemistry, the contrast occurs between the intramolecular directed covalent bonds, and the intermolecular hydrogen bonds which generate the solid. Two recent examples (21, 22) illustrate this point. For instance, the structure of the 1:1 adduct between melanine and cyanuric acid (Fig. 7a) is completely governed by the positions of the electronegative atoms and the hydrogens. The shape of the molecule also determines the dimensionality of the interactions: the planar configuration of both molecules implies only two-dimensional strong hydrogen bonds, whereas weak van der Waals interactions in the third dimension lead to the stacking of the layers giving rise to the solid.

Several routes are used by molecular chemists to create the three-dimensional solid. The most famous is supramolecular chemistry (23) which uses the coordination power of cations toward oxygen, nitrogen, and sulfur atoms belonging to organic molecules to realize an extended solid. By creation of ionocovalent bonds, cations act as “knots” between the organic entities. Here also, the shape of the latter is decisive for the dimensionality of the resulting structure, but the nature of the coordination polyhedron around the cation is also important. It is pure design. A nice and recent example of that is provided (Fig. 7b) by the triflate of silver tricyanobenzene (24).

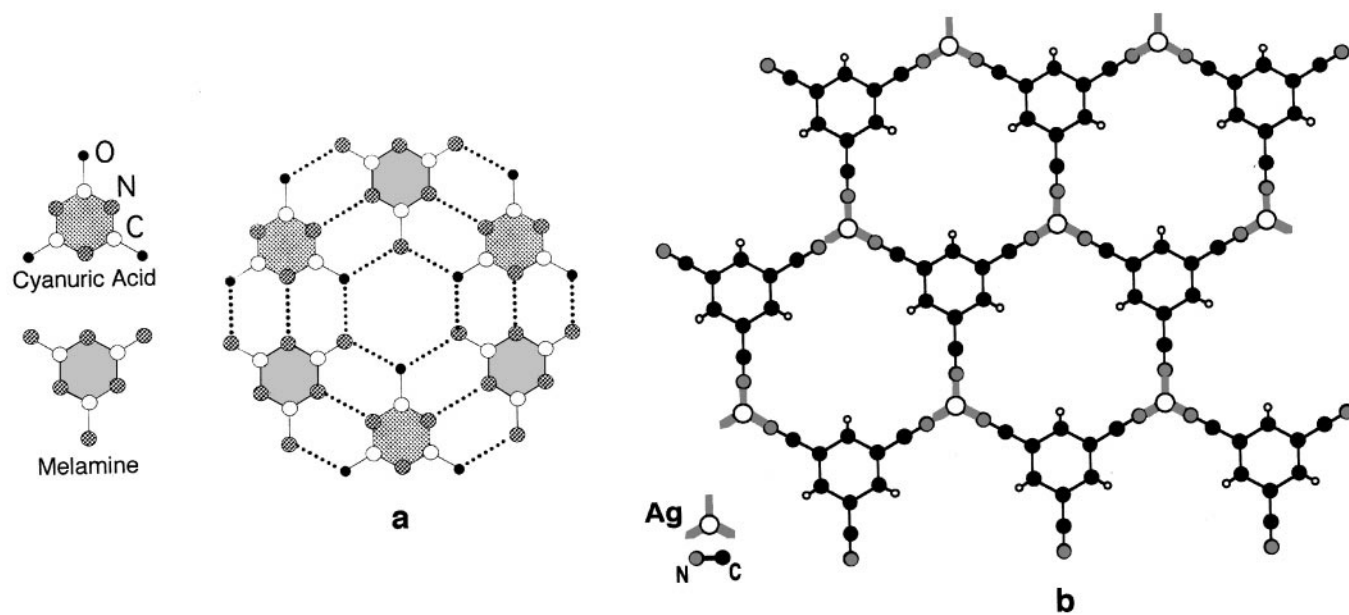


FIG. 7. (a) Layered structure of the 1:1 melamine–cyanuric acid adduct, with hydrogen bond linkage. (b) Layer of the Silver tricyanobenzene triflate, formed by ligation by cyano groups around Ag via ionocovalent bonds; the triflate ions, located at the center of the hexagonal cavity, are omitted for the sake of clarity.

Increasing the complexity led in particular Achim Müller (25) to combine several building units containing the same cation, which coexist in the solution for building finite objects: the “giant wheels” which can further act themselves as BUs in a “powers of ten” condensation of these giant species to try to generate the infinite solid, by a very elegant chemistry. He builds the Renaissance castle and the Pisa tower!

Another elegant way of obtaining rational design of solids is explained in detail in this issue (26). Starting from one BU (here, the $[\text{Mo}_2\text{O}_2\text{S}_2]^{2+}$ ion) known in the solution, Sécheresse *et al.* use the properties of oligomeric condensation of this polycation to build in the solution neutral or anionic wheels differing by their nuclearity, shape, and charge. The solids are then derived by tuning the type of associated cation which creates solids with dimensionality ranging from 0 to 3.

Reactions under hydrothermal conditions. As already stated, almost nothing is known for these conditions. The drastic change in the properties of the solvent (dielectric constant, polarizing power, weaker association between the solvent molecules, ...) affects the nature of the species in the solution, and what was possible at room temperature from the knowledge of the species in the solution becomes impossible. Compared to supramolecular chemistry, hydrothermal synthesis is a “black box” in which one enters the reagents and observes the products. When one knows the richness of this synthesis procedure and the fields in which it is applied (zeolites in particular), it is necessary to

open the box. The same work as that done in the 1960s for solutions at room temperature has to be realized under hydrothermal conditions. Only a few groups (10, 27–30) have begun this approach on aluminates and metal phosphates by an extensive use of *in situ* solid and liquid NMR and *in situ* synchrotron facilities adapted to follow the reactions under the true conditions of the synthesis. The present state of the art, mainly established from the study of the formation of porous fluorinated metal phosphates ($M = \text{Al}, \text{Ga}, \text{Ti}$), shows that the BUs in the solution are formed by the oligomeric condensation of prenucleation building units (mainly metal monophosphate complexes). The BUs formed during the nucleation process have shape and metal coordination close—but not identical—to that of the BUs from which the three-dimensional can be described. Moreover, it seems that the density of charge of the counterion (here, diprotonated amines) has a key role in all the process. In the solution, it controls the extent of oligomeric condensation of the prenucleation units which stops when the density of charge of the BU and of the amines become equal; it gives rise to neutral ion pairs BU–amine. These pairs connect to each other by ololation or oxolation reactions and lead to the precipitation of the solid. This process seems to be valuable whatever the nature of the porous solids (micro- or mesoporous). Indeed, it was recently shown (31) by *in situ* solid and liquid NMR that the synthesis of micro- and mesoporous titanium phosphates was driven by the same tetrameric BU in the solution. The BU contains two titanium octahedra and two phosphates and

little change occurs in its structure during the formation of the microporous solid. Owing to the structural disorder in the walls of mesoporous compounds, such a comparison was not possible for the mesophase.

These first results seem to show that, in contrast to supramolecular chemistry, there is no invariance of the species in the solution and in the solid. This type of chemistry needs to be much more explored and it is reasonable to think that, in the future, hydrothermal supramolecular chemistry will also lead to designed solids.

3. BUILDING UNITS AND “SCALE CHEMISTRY”

3.1. Size and Nets

The beginning of this paper concerned building units as means of structural description and/or active and real bricks for the edification of the solid. It did not really take into account their compared sizes nor the topology of their stacking. Such a comparison is unusual, but rich. It was already stated that many BUs are polyhedral clusters (12). The BU can be the atom itself, the anionic polyhedron around a metallic center, or an association of polyhedra, identical or different, and their linkage in the solid can be weak, medium, or strong. Whatever the strength of the inter-BU bonding, a careful look at many structures shows that the assembly of these BUs adopts in many cases the topology of the very simple structures that every student knows. To get such a look at these structures, one must consider every BU as a single entity. Take for example polonium metal (Fig. 8a). It adopts a simple cubic P lattice, the atoms on the edges being in contact. If you replace each atom by an octahedron, keeping the same type of contacts, the famous ReO_3 structure is obtained. The same topology is observed if corner-linked tetramers of two phosphate and two octahedra replace the octahedron: this is the case for $\text{AlPO}_4\text{-CJ2}$ (32) and even for the Linde A zeolite where each BU (Fig. 8a, bottom) contains 24 tetrahedra!

This observation is not restricted to the P lattice. Figs. 8b and 9a,b show examples for the I and F lattices. We could also have represented in Fig. 9a the fullerene structure, but as the atoms are represented at the same scale, the figure would have been too large. That means that, whatever the size of the BUs, their spatial arrangement is the same as for simple structures. It is what I suggest to call “scale chemistry”: the arrangement of BUs is the same; only the size of the cells changes. That means also that the concept of nets (see for instance (33)), which was initially applied to simple structures, also applies here and authorizes the discovery of new topologies, the BUs replacing the vertices of the nets.

3.2. Scale Chemistry in Structure Types

This observation also applies to structure types. For instance (Fig. 10), the well-known barium niobate BaNb_2O_6

and calcium tantalate CaTa_2O_6 , which have a pair of edge-shared octahedra as BUs, have an upper analogue with the structures of ULM-3 and ULM-4 (34, 35), two fluorinated gallophosphates in which the BUs are the SBU-6 hexamers containing three phosphate groups, and three gallium polyhedra (one octahedron and two trigonal bipyramids) already described in Fig. 6.

The most impressive example concerns the sulfides ASU-31 (Fig. 11) and ASU-32, recently discovered by Yaghi and O’Keeffe (36). Other groups, like those of Parise (37) and Ozin (38), were interested in supertetrahedra. Indeed, starting from structures based on single MX_4 tetrahedra, others are built from assemblies of four corner-shared tetrahedra ($(\text{Ge}_4\text{S}_{10})^{4-}$ ions), labeled T2, or 10 corner-shared tetrahedra ($(\text{In}_{10}\text{S}_{20})^{10-}$ ions), labeled T3. The corresponding BUs, linked by corners, create three-dimensional solids, either dense or related to the β -cristoballite structure or also built from two interpenetrated subnetworks (see references of the structure types in (12, 36–38)). The unique character of ASU-31 and ASU-32 is that the T3 BUs are arranged in a zeolitic topology. It is, at the third stage, the homologue of tetrahedrite, a distorted variant of the sodalite structure for ASU-31 and of the CrB4 net for ASU-32, leaving cage diameters of 25.6 and 17.2 Å respectively! This time, it is the building of pyramids with very big stones!

The HTB structure topology is found (Fig. 12) using bricks as different as single octahedra, SBU-6 hexamers (in MIL-HTB described above), tetramers of edge-sharing octahedra in MIL-16, a porous cobalt succinate (39), and even the three-dimensional intercalation complex between idarubicine and the hexanucleotide d(CGATCG) (40), in which the size of the channel becomes more than 36 Å!. The example of the cobalt succinate has the advantage of showing that the resulting topology is independent of the chemical objects used for the synthesis. Indeed, since the beginning of this paper, the BUs were either organic or inorganic, but the combination of the two types of bricks leads also to infinite hybrid solids related to known structure types and, if the anisotropy of the organic part is important, this leads to pillared solids (the Pisa tower!!).

In this field of hybrid solids, using their knowledge of both the metal’s coordination preferences and ligand geometry, some groups have succeeded in producing “molecular minerals” of several three-dimensional structure types including PtS, NbO, rutile, and quartz (41–44). Very recently, with the same idea, Keller and Lopez (45) discovered an extraordinary coordination solid which is the upper homologue of nekoite, a layered silicate mineral with pentagonal cavities.

All these examples are very strange, having the same topology, whatever the nature and the size of the BUs. A thermodynamical question arises: why? Roughly speaking, it seems that the edification of the solid would result in

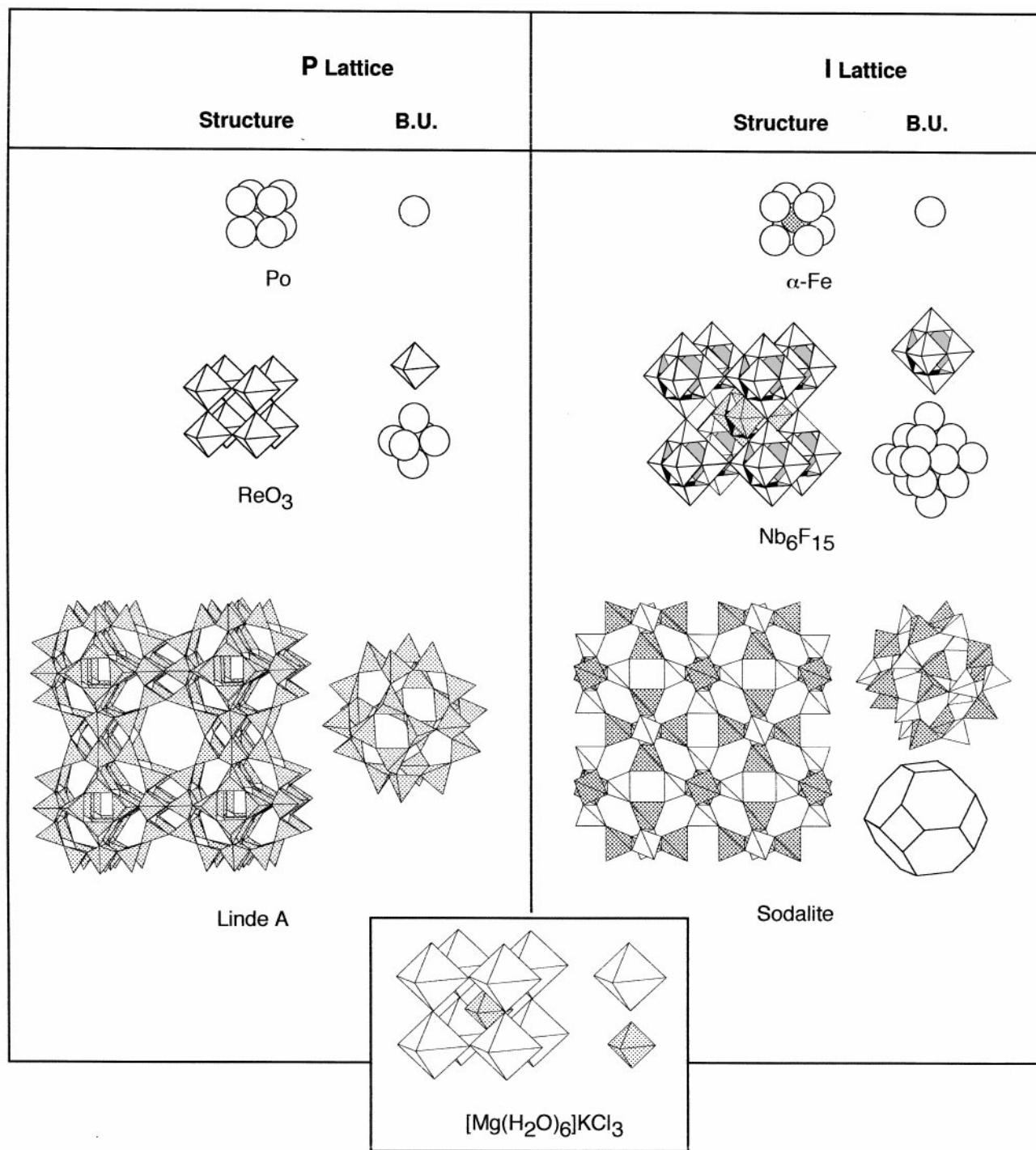


FIG. 8. Homothetic arrangement of building units in some structures with P (a) and I lattices (b).

two types of energy: the “internal energy” which would correspond to the edification of the brick, which would be roughly proportional to the size of the brick, and a quasi constant “linkage energy” between the bricks. It is clear that, in such a preliminary proposal, the energy

of interaction between the framework and the occupied species is not taken into account. This general remark could be considered as nonsense by classical experts in thermodynamics, but these examples, at least, ask the question.

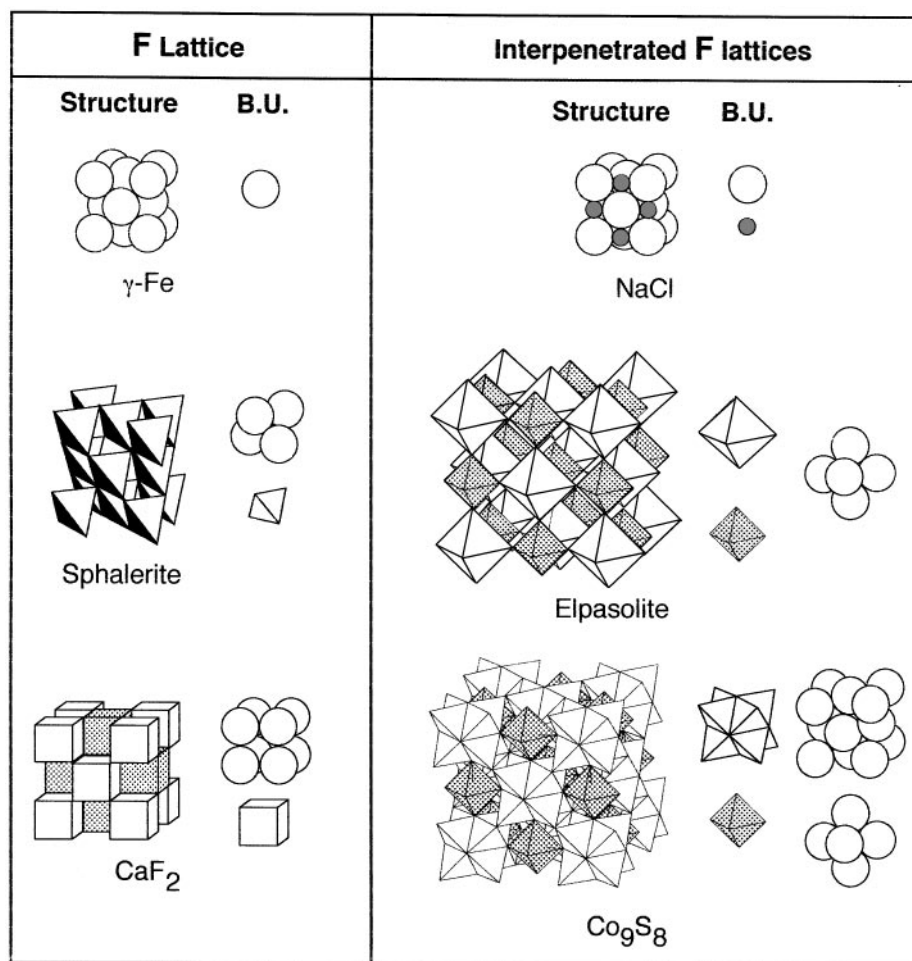


FIG. 9. Homothetic arrangement of building units in some structures with an F lattice (a) and two interpenetrated F lattices (b).

3.3. Scale Chemistry and Holes

Increasing the size of the BUs has also an advantage. The cavities created by the framework, which were very small in the usual solid-state inorganic frameworks, and only able to accept alkaline and/or alkaline-earth cations, become larger and larger, and the need for giant pores, that we recently claimed with Tony Cheetham (46), is finding solutions. Compared to the world of zeolites and microporous compounds (47) we have now some examples of gigantic pores, much larger than the usual zeolites. They originate from pure inorganic (cages in indium sulfides (36), tunnels in nickel (48), or zinc phosphates (49)) or hybrid organic-inorganic frameworks (see for instance the last beautiful discovery of Zubietta in (50) of a perovskite-related solid in which occluded K^+ cations are replaced by the aggregate $\text{FeMo}_6\text{O}_{19}$). But, for what purposes?

Indeed, this is not only a game for topological chemistry. Clearly, the roles that zeolites play in catalysis, separations,

and ion exchange processes can be kept, but using larger and larger molecules; the design of tailored materials with large BUs can lead to new applications, for example, in sensors and nanotechnology, with better performances than mesoporous solids, owing to their better thermal stability. They can act also, and I think this will be their best application in the future, as chemical reactors at the nanoscopic scale, the size of the cavities allowing special reactions between large molecules in a confined space.

Beside the dream, Achim Müller has shown two fascinating consequences of having large pores:

(i) The giant wheels he described could accept large species within the hole, and starting from the Mo_{176} wheel, he was able to cap it by two Mo_{36} units to give the Mo_{248} moiety, but a careful look at what happened inside clearly showed that the organization of the Mo_{36} units in the confined space was very similar to that of the pure molybdenum oxide Mo_5O_{14} (25). In other words, Müller showed for the first time that the use of large holes allows us to

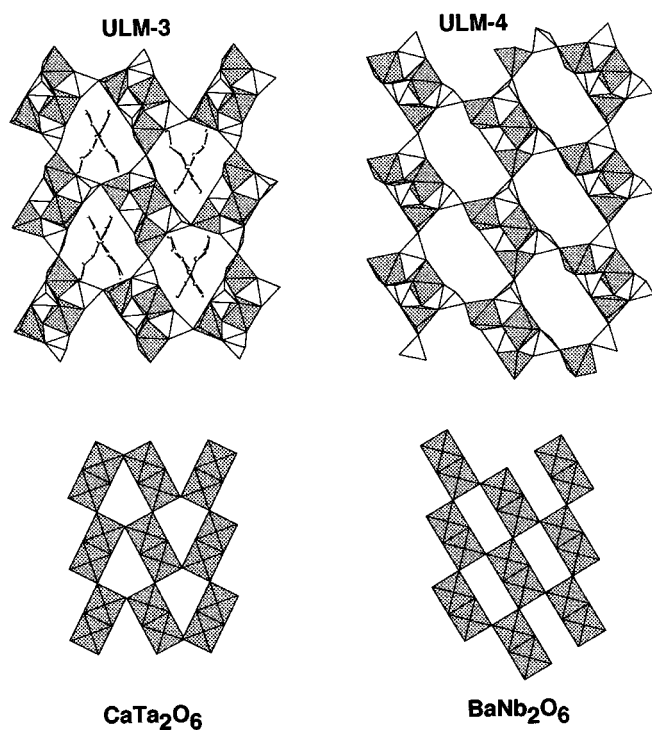


FIG. 10. Relation between ULM-3 and CaTa_2O_6 (left) and between ULM-4 and BaNb_2O_6 (right).

mimic the nucleation and growth of usual solids by a “ship in the bottle” process.

(ii) In his continuous success in synthesizing giant objects, he recently described (51, 52) new spheres and baskets based

on pentagonal BUs and, most importantly, the new type of anionic exchange occurring between ligands and/or guest molecules within these giant polyanions. There is really no limit to the creation of these giant objects, except, perhaps, our imagination.

4. BUILDING UNITS, “SCALE CHEMISTRY,” AND TRENDS: CONCLUSION

We tried to prove that the concept of building units is very useful for the creation of new species, unexpected without its aid. Two orientations appear now. Starting from the notion of bricks, the topology of their arrangement is not arbitrary and always results from a minimization of the lattice energy during the condensation of the bricks. That means that simulation and prediction can be possible starting not from the atoms as usual, but from the predetermined BU. We recently initiated (53) such an approach (which is new to our knowledge) with purely inorganic structures, starting from simple polyhedra (tetrahedra and octahedra), or complex building units (bioctahedra, tri-, tetra- and tetramers of octahedra, and even mixed tetrameric building units (two tetrahedra and two octahedra)). With this simple approach, we were able to find not only the classical structure types (ReO_3 , perovskite, TTB, HTB, pyrochlores, niobates and tantalates for octahedra-based structures, some zeolitic frameworks with tetrahedra, ...) but also unknown networks with an excellent thermodynamical stability. The game, which is currently in progress in our group, will be to imagine the “*a posteriori*” chemistry which provides these unknown structures. The feasibility of this step being

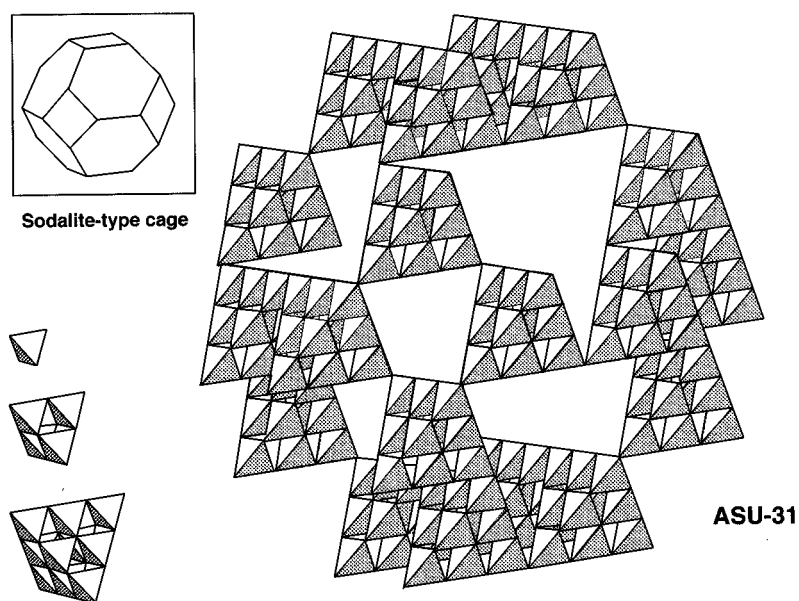


FIG. 11. Perspective view of ASU-31 (from (36)) with the T1, T2, and T3 units (see text) and the sodalite cage (from (36)).

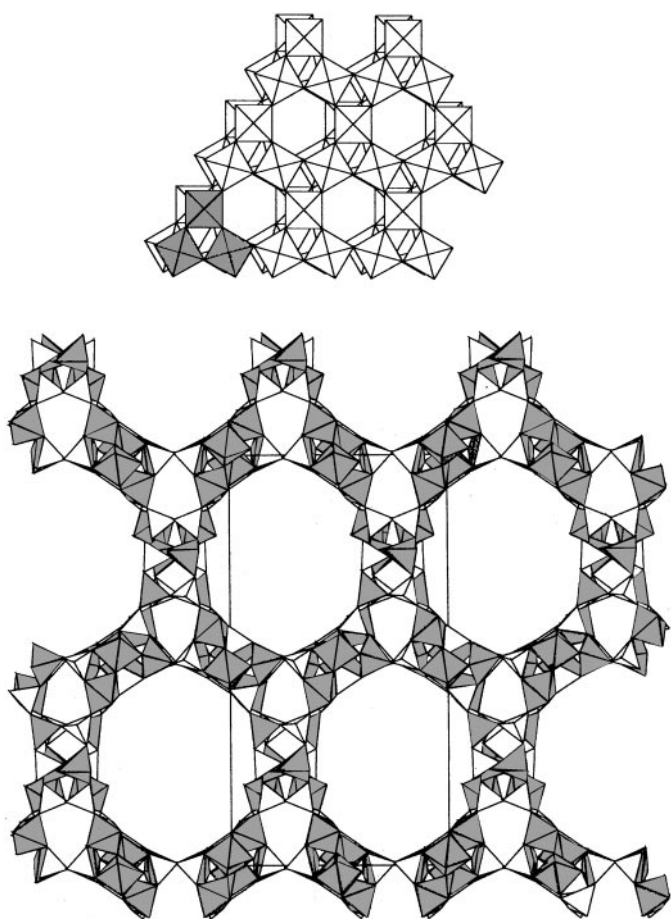


FIG. 12. Enhancement of the HTB topology from single octahedra as BUs to hexamers.

established, we shall increase the complexity with new types of BUs and try to find other unknown structures, the challenge being to invent chemistry dedicated to each of them.

The second trend that I see is to systematically introduce the physical property within the BU, and here also, the domain is immense. For instance, is it possible to create infinite networks based on polyoxoanions, defective or not, which are well known to be electron “pumps.” The resulting solids would be excellent candidates for electrochemical devices.

Finally, the present research based on the concept of building units is very powerful, and the question is not now “What is possible?” but rather “What is impossible?.” Once more, J. M. Lehn was right: there is only one chemistry, and I could say one *structural chemistry*. We have shown that, topologically, it seems that there is a *continuum* from structural organic, hybrid, and inorganic structures in their three-dimensional arrangement (Fig. 13). If we can enhance this approach, unbelievable and unexpected properties will emerge. For that, first, rational chemistry is necessary. Just do it!

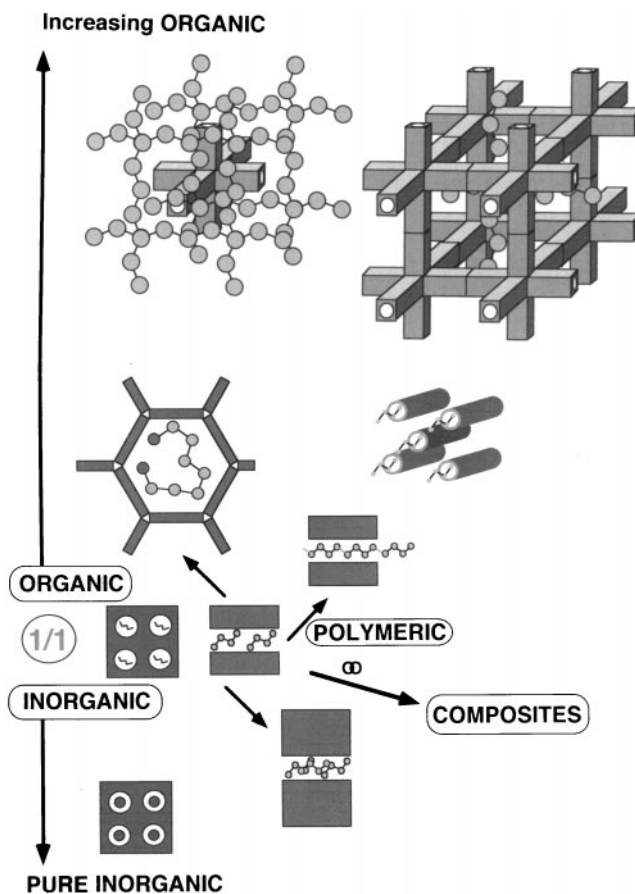


FIG. 13. Continuum between organic and inorganic frameworks. The latter are shown in dark gray, and the former are represented by spheres and chains.

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