

ARTICLES

Crystallized Frameworks with Giant Pores: Are There Limits to the Possible?

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ABSTRACT

In the domain of porous solids with inorganic or hybrid frameworks, the combination of mastered chemistry and of computer simulations pushes forward the limits of the classical approach and allows the full determination from powder diffraction data of architectures with cells of several hundred thousand cubic angstroms with hierarchies of giant pores and unprecedented Langmuir surfaces. The different limits induced by this new approach are analyzed.

1. Introduction

In materials science, the search for new porous solids, either with an inorganic or with a hybrid organic–inorganic framework, is very topical,¹ fueled by the strong incentive related to their use in catalysis, gas separation,² or strategic gas storage.^{3–6} Indeed, when compared to other materials, porous solids are unique. They alone exhibit at the same time (i) a framework responsible, as in dense solids, for physical properties such as magnetism, conductivity, and optical features, (ii) pores that can store species, and (iii) an internal surface that is at the origin

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of the catalytic properties of these materials. Following the intense development of inorganic frameworks in the early 1990s,⁷ a new class of materials has emerged at the crossroads of inorganic materials science and coordination chemistry:⁸ the hybrid porous solids or metal–organic frameworks (MOFs), in which the framework is ensured by the linkage of inorganic moieties (mono- or oligomeric) with functionalized organic molecules through covalent or iono-covalent bonds.^{1,9–16}

In both subclasses (inorganic or hybrid skeletons), a tremendous variety of systems were chemically and structurally tested. However, it rapidly became necessary to introduce rational approaches besides these “trial and error” experiments with the aim of reaching tailor-made structures for specific applications. For templated inorganic frameworks such as silicates, metal phosphates, metal halides, or chalcogenides, mainly obtained under hydrothermal conditions (200 °C, 10–30 bar), an approach to their mechanisms of formation was needed to play further on conditions of synthesis for obtaining the desired product. For hybrid frameworks, which combine an inorganic part (single polyhedra, clusters, or chains) and an organic moiety, the directivity of the covalent bonds introduces more initial geometric information as soon as the inorganic brick is known and stable. Moreover, whatever the subclass, another challenge^{17–19} was to increase the size of the pores, limited 15 years ago to ca. 10 Å in diameter. Indeed, larger pores imply enhanced specific surfaces, an important parameter for catalytic properties, and more possibilities for the storage of species. This last point becomes more and more crucial in the 21st century where problems of sustainable development will increase dramatically.

The challenge of large pores is relevant to “molecular gigantism”^{14,20–22} and will concern exclusively microporous solids (pore diameter < 20 Å) in this paper. The mesoporous solids will not be considered. They have much larger pore diameters, but their amorphous skeletons rules out their characterization at the atomic scale.

Five years after these questions, many of the above problems have been solved thanks to the two concepts of “scale chemistry”²⁰ for templated inorganic porous solids and the “reticular chemistry of augmented nets”¹³ for MOFs. Both of them use the concept of secondary building units (SBUs). However, in both cases, despite some successes in obtaining giant pores, limitations appeared. They are of a chemical nature because either the chemistry of the desired solids is not yet possible or the lack of single crystals rules out any structural determination. Until recently, these limits implicitly restricted identifications of new frameworks. After a description of the state-of-the-art in the domains of inorganic and hybrid

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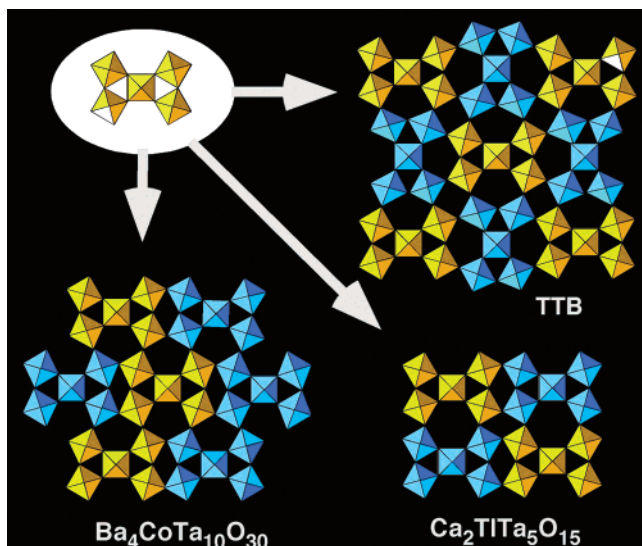


FIGURE 1. Some tungsten–bronze-related structures based on the same pentameric SBU.

porous frameworks, we shall show that the combination of a mastered chemistry and *de novo* computer simulations of framework topologies pulls down this limit and allows the synthesis and the structural characterizations of solids with giant cells ($700\,000\text{ \AA}^3$) from powder diffraction data. A hierarchy of nano- and mesopores was identified in a single crystallized compound with outstanding sorption properties. The gap is important, but the open doors show simultaneously new and unprecedented limitations, which are discussed at the end the paper.

2. Templated Porous Inorganic Solids

They are obtained by precipitation in hydrothermal conditions from an aqueous solution, which contains, besides the inorganic species, organic moieties such as amines or ammonium ions acting as templates during the precipitation. Zeolites² are the most well-known of this category. Their framework, based on corner-sharing of SiO_4 and AlO_4 tetrahedra, delimits cages, tunnels, or both, which represent the pores of the structures. Later, other porous solids⁷ (metal phosphates and arsenates, halides, and chalcogenides) involving not only tetrahedral but also pentahedral and octahedral coordinations for the metals were discovered. Instead of the connection of simple polyhedra, the crystal chemistry of all these structures is better described from secondary building units (SBUs), which represent the maximum assembly of polyhedra of which the connection in the three dimensions of the space restores the structure (Figure 1).

SBUs, Mechanisms of Formation, and Simulation of Structures. The concept of a SBU was a useful tool for the *description* and classification of the porous structures, but there was no experimental proof of their real existence in the solution. The dogma was the invariance of these SBUs during the precipitation process. Attempts to rationally create new topologies needed a verification of this hypothesis. Our group made it on porous alumino- and

gallophosphates²³ and titanophosphates²⁴ using *in-* and *ex-situ* NMR experiments in the conditions of hydrothermal synthesis. The existence of the SBUs in the solution were confirmed for these systems, and it was proved that the driving force of the synthesis was the charge density of the template, which (i) governs the extent of the oligomeric condensation, which gives rise to the SBU in the solution, (ii) is responsible for the creation of neutral ion pairs leading to precipitation, and (iii) determines, by its size and plasticity, the structural organization.

Once the existence of the bricks was established, and therefore the chemical conditions of their stability, it became possible to create new materials based on a given brick by playing on the nature of the amine template. It was an approach to tailor-made solids (the fashionable term “design”, which will be discussed at the end of the paper, is avoided), with some successes.^{25,26} It was however clear that it is impossible for chemists to explore the whole space of phases in a system. So, we introduced an original computer simulation method for generating candidate crystal structures (automated assembly of secondary building units or AASBU method),²⁷ based on the concept of SBUs and their linkage in 3D space. For a given brick, the AASBU method produces virtual libraries of energetically viable inorganic structures based on a predefined SBU. These bricks are implemented according to the following criteria: (i) one constraint on the nature or size of the SBUs involved, $M/P = 1$ for AlPOs and GaPOs; (ii) no explicit constraints on cell dimensions but, optionally, on space group symmetry; (iii) an ability to accommodate one or more types of SBUs; (iv) accommodation of differing modes of inter-SBU connection, allowing, for example, corner-, edge-, and face-sharing modes; (v) a broad flexibility in the definition of the linkage points. The wide applicability of the method in inorganic chemistry was demonstrated by finding the known families of inorganic structures using simple SBUs. It also provided numerous hypothetical frameworks (Figure 2) using several types of SBUs,^{28,29} which were classified as not-yet discovered or virtual^{29,30} according to their relative energy compared to that of dense phases. Chemical studies are currently in progress to discover some of them.

SBUs and “Scale Chemistry”: A Route for Large Pores.

The examination of many inorganic structures with different complexities led one of us²⁰ to show that, despite increasing the size of the *descriptive* SBU, the topology of the resulting frameworks remained invariant and referred to the classical dense structures of the solid-state chemistry. This had a direct consequence for the search for large pores. Indeed, if it is possible to create large SBUs instead of the small ones discovered until now, larger SBUs would create larger pores, which is one of the challenges in the field of porous compounds. Owing to the special role played by the charge density of the amine on the size of the SBU (lower the charge density, larger the SBU; see, for instance, ref 2, Vol. 2, p 858], the search for large pores required the use of large, multifunctional amines with weak protonation for obtaining for them a low charge density and initiating a large SBU. Recently, our group

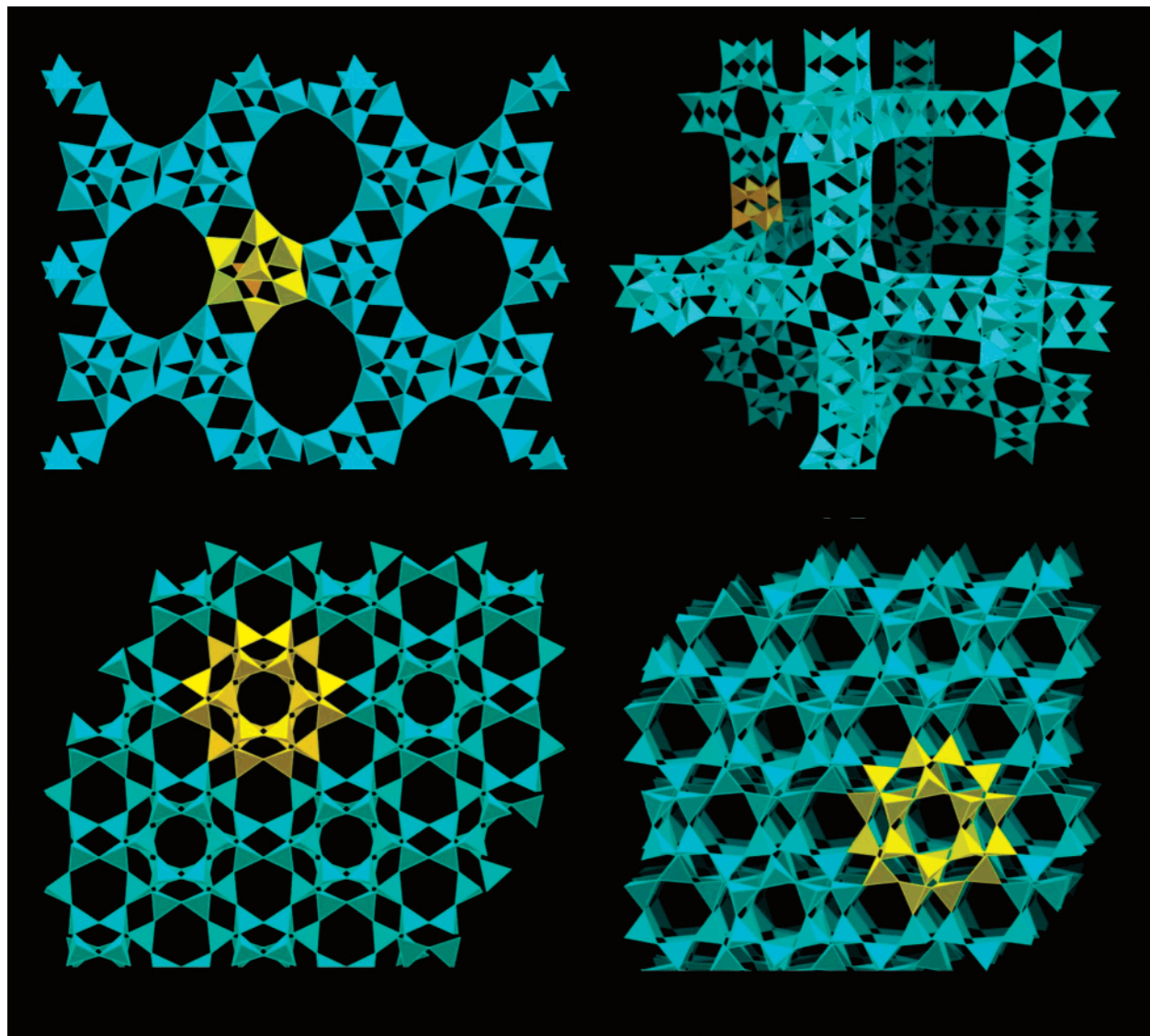


FIGURE 2. Some hypothetical frameworks based on a double-four-ring unit (D4R) [top] and on a sodalite cage [bottom]. The SBUs are highlighted in yellow.

demonstrated this approach with an aluminophosphate using TREN as templating agent.³¹ It adopts a supersodalite framework (Figure 3) in which the usual tetrameric squares of tetrahedra are replaced by enneamers. The hexagonal windows of the sodalite structure become dodecagonal and create a large cage, eight times that of the sodalite. At its center is trapped an unprecedented cluster of 17 water molecules, which reversibly evolve the structure, leaving voids (\emptyset , 10 Å), which can be occupied by other species.

Scale chemistry applies also to a fascinating new family of templated porous indium-metal chalcogenides coming from two American groups.³² The structures are all based on T_p supertetrahedra, which are formed by the corner-sharing of single InX_4 tetrahedra, p (currently ≤ 5) corresponding to the number of single tetrahedra along one edge of the supertetrahedron. The latter share vertices and the cages, which are occupied by the templates. Moreover these supertetrahedra can assemble into hypertetrahedra labeled $T_{p,q}$ for the description of a T_q hypertetrahedra

composed of T_p supertetrahedra. If the templates could leave the cages, this would provide a free volume of more than 1800 Å³! Unfortunately, the extraction of the amine leads to a collapse of the structures. Finally, all these phases confirm the statement described in ref 20 since they represent the upper homologues of dense structures such as diamond, sodalite, cristoballite, and CrB_4 types.

First Limits. The above examples show some limits in the evolution toward large cavities in porous inorganic solids. Chemically, it seems that in some systems the reactivity of the components decreases with the complexity of the SBU and, even if some topologies can be predicted, the possibility of obtaining the corresponding solids becomes sometimes doubtful. Moreover, it is well-known that as soon as the cell volume of a structure increases, it is more and more difficult to get single crystals, which is a key point for the structural characterization of the synthesized compound. This is already true for protein crystallography. Concerning inorganic chemistry and despite the tremendous progress in ab initio

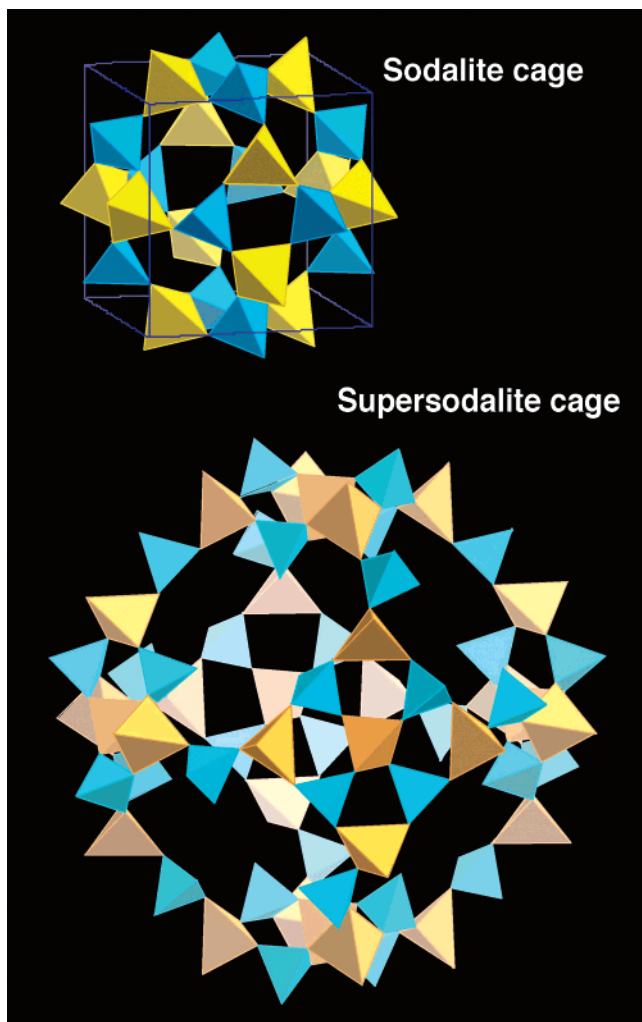


FIGURE 3. The sodalite structure [top] and supersodalite structure of $Zn_3Al_6(PO_4)_{12}$, 4 TREN, 17 H_2O obtained using the “scale chemistry” concept (see text).

structural determination from powder diffraction data, a crystal is necessary for structures with large cells (see sulfide³³ where the cell volume is superior to $100\,000\text{ \AA}^3$). Another consequence of this increase in the dimensions of the pores is the related decrease of thermal stability when the template is extracted. Whereas in zeolites and most aluminophosphates the evacuation of the template maintains the integrity of the skeleton, a collapse of the structure is more and more frequent when the pores become larger. Some of these limits, which restrict the field of new porous inorganic compounds, do not exist for hybrid solids, as it will be shown now.

3. Porous Metal–Organic Frameworks (MOFs)

The State of the Art. MOFs and porous metal phosphates convey the same concept, the organic part taking the place of the phosphate ion within the framework. This formal substitution dramatically increases the number of possibilities, owing to the infinite variety of organic molecules that can be used. They must however possess chelating functionalities. The most used are polycarboxylates, polyphosphonates, and polysulfonates with either aliphatic or

rigid carbon skeletons, which are fixed by ionic-covalent bonds to the metallic centers. Within the hybrid 3D network, if this inorganic part is zero-dimensional (single polyhedra or clusters), one speaks about coordination polymers. They represent the major part of the discovered solids, up to now. More rarely, however, the dimensionality of the inorganic subnetwork can also be 1D,^{34,35} 2D,^{36,37} and even 3D,^{38–40} and it was recently shown⁴¹ that within a given system the reaction temperature plays a major role in the degree of condensation of the inorganic subnetwork, which can range from 0D to 3D in a few tenths of a degree. If one adds that the reaction of the organic ligands is effective with almost all the metallic elements including transition metals and rare earths, the result is the discovery of hundreds of new compounds over the past 10 years. Compared to the solids with a pure inorganic skeleton, which require the extraction of the template to become porous, MOFs have the great advantage to give directly accessible porosity after extracting the solvent molecules, modulable by the size of the ligand. They have however, in most cases, a lower thermal stability than inorganic frameworks.

Once the richness of the field was discovered, it was necessary to rationalize the synthesis of the MOFs to provide tailor-made architectures. In five main seminal articles,^{3,13–15,42} Yaghi and O’Keeffe and co-workers progressively defined the *reticular chemistry* concept with the chemical and topological rules governing this possible design. This concept starts from the formation in the solution of well-defined and rigid inorganic and organic building blocks, which must maintain their structural integrity throughout the construction process of the solid. The proper choice of these inorganic and organic building blocks and their assembly by strong bonding is deemed to lead to predetermined ordered structures, reminiscent of the topology of dense structures. Numerous examples in the literature illustrate now this concept, the most famous being MOF-5 and its derived structures.³

However, there are two difficult steps in this strategy. The first is the chemical control of the existence of the inorganic SBU, mainly in solvothermal conditions. These SBUs are well-known by the inorganic chemists for room or moderate temperatures of reaction. On the contrary, nothing is established as soon as hydrothermal conditions are applied because the properties of the solvent change drastically and therefore the nature of the species in the solution. A systematic study of the conditions of the existence of each SBU is therefore needed before applying the concept of reticular synthesis. Moreover, as far as the search for giant pores is concerned, the second difficulty comes from the tendency of the framework to be interpenetrated or interwoven,¹⁰ which decreases the porosity of the solid and must be avoided, when possible.

Besides these difficulties, the reticular chemistry principles, which aim at the “design” of MOFs, merit two types of remarks, which both respect the generality of the edicted rules. The first is chemical and concerns the illustrations of the concept. The number of examples that will confirm it are strongly dependent on the possibilities

of obtaining single crystals, and it may be anticipated that the difficulty in getting them will drastically increase with the size of the pores. It will more and more imply the use of the difficult *ab initio* structural determinations from powder diffraction data. The second is that reticular chemistry concerns only the realization of a reasonable expectation, based on intuition, of a given architecture. It does not explore *all the possibilities* of connection of the appropriate inorganic and organic building blocks. In particular, it does not predict polymorphs. Only original global optimization simulations, like those that we performed on inorganic skeletons (see above), are appropriate to an exploration of the whole space of configurations.

A New Method. With these ideas, our group developed a new method⁴⁵ respecting the reticular chemistry principles. It combines the determination of the chemical conditions of existence and integrity of the inorganic SBU in solvothermal medium⁴³ and a computer simulation approach for the prediction of hybrid structures.⁴⁴ The latter uses a simulated annealing Monte Carlo procedure and generates the whole set of possible connections between organic and inorganic SBUs. If there is a reaction between the organic and inorganic counterparts, the resulting product must adopt one of the virtual structures obtained from the simulations. Moreover, just the comparison between the experimental and the calculated powder diffraction patterns provides the structural solution.

For being credible, our chemical approach aimed at originality and concerned the search for the conditions of stability of a trimeric inorganic unit (a scarce SBU reported only with divalent cations) but with trivalent ions for which no example exists up to now in the domain of MOFs. Our strategy was to start from soluble precursors that already contain these trimers and to establish the conditions for its chemical integrity during the reaction. These conditions, primitively determined for Fe³⁺, have been extended recently⁴⁵ to Cr³⁺ and V³⁺ and lead to new MOFs that contain the desired SBU.

Our simulation method takes advantage of the SBU concept used in our previous AASBU method,²⁷ through the assembly of predefined organic and inorganic SBUs. It is performed in 3D space with minimal input, aiming at computationally exploring the possibilities of connection. The inorganic and organic counterparts may be treated independently, that is, as two different building units (the “mixture” method in ref 44) or encapsulated in a single hybrid building block. Both approaches were explored. The simulations provide a list of hybrid candidates with their space group, cell parameters, and atomic positions. Our motivations aims not only at simulating existing structures but more importantly at predicting not-yet-synthesized structures, aiding the often difficult task of crystal structure determination, rationalizing different but related structure types, while tackling the issue of polymorphism by limiting the domain of structures that are possible for a given metal–organic ligand pair.

The preliminary step consists of elaborating a suitable library of SBUs, directly extracted from known MOFs. The

inorganic unit is modeled as a rigid body and the organic unit as a flexible body. The computational assembly is further controlled through the use of predefined “sticky-atoms”: all ligand atoms on both units being defined as equally possible linkage points. The rules that control the possible assembly of the two SBUs during the subsequent simulation steps are defined in a force field that includes “sticky-atom” *pairs*, parametrized on an atom–atom basis by a simple Lennard-Jones expression for the “energy” of interaction. A repulsive potential between organic pairs avoids their overlapping. For a run, the amount of input data is minimum: the number of organic and inorganic units per asymmetric unit and, optionally, the space group.

The validity of the method was proved by finding the existing and well-characterized MOFs based on mono-, di-, and tetrameric inorganic SBUs and organic ligands such as benzene 1,4-dicarboxylate (BDC) or benzene 1,3,5-tricarboxylate (BTC) with a very good accuracy. However, the most attractive feature of the simulations remains the generation of new topologies (Figure 4).

Breakthroughs. The application of the method to trimeric units with the same ligands as above (BDC and BTC) in a 1:1 ratio for BDC and 2:3 for BTC leads to a whole series of plausible and very open metal–organic frameworks with hitherto unknown topologies for most of them. Two of them are of particular interest for the unprecedented giant cells that they provide (380 000 and 706 000 Å³), far beyond all the known ones. Last but not least, the Bragg peaks of their calculated diffraction pattern exactly fit with those of solids (MIL-100 for BTC and MIL-101 for BDC) obtained in a powdered form in the systems Cr(III)-BDC and Cr(III)-BTC for a 1:1 Cr/BxC ratio (x = D or T). The only difference concerns the discrepancy between calculated and experimental intensities, the first corresponding only to the skeleton, whereas the experimental also taking into account the contribution of the occluded species. Astonishingly, despite the large number of parameters (>200 for BTC), the Rietveld refinement of powder data, obtained using synchrotron radiation, converges toward good *R* values and improves the prediction by the location of the inserted species, that is, free water molecules in the case of MIL-100.

The resulting cubic structures (space group *Fd $\bar{3}m$*) have in common (Figure 5) the occurrence of supertetrahedra as building blocks, formed in such a way that the four vertices of the supertetrahedra are occupied by the trimers. Depending on the nature of the organic linker, the position of the latter corresponds to either the edges (BDC) or the faces (BTC) of the supertetrahedra (ST) (Figure 5b,c). Within it, the cage, which is limited by 24 oxygens and either 48 (BDC) or 36 carbons (BTC), corresponds to free internal diameters of 8.7 and 6.6 Å, respectively. These dimensions correspond to the domain of *micropores*, in the same range as zeolites. More interestingly, the corner-sharing of the ST delimits a framework with two types of cages (Figure 2d,e), the dimensions of which are now typically in the range of *mesopores*. With BTC, the smallest one, limited by 20

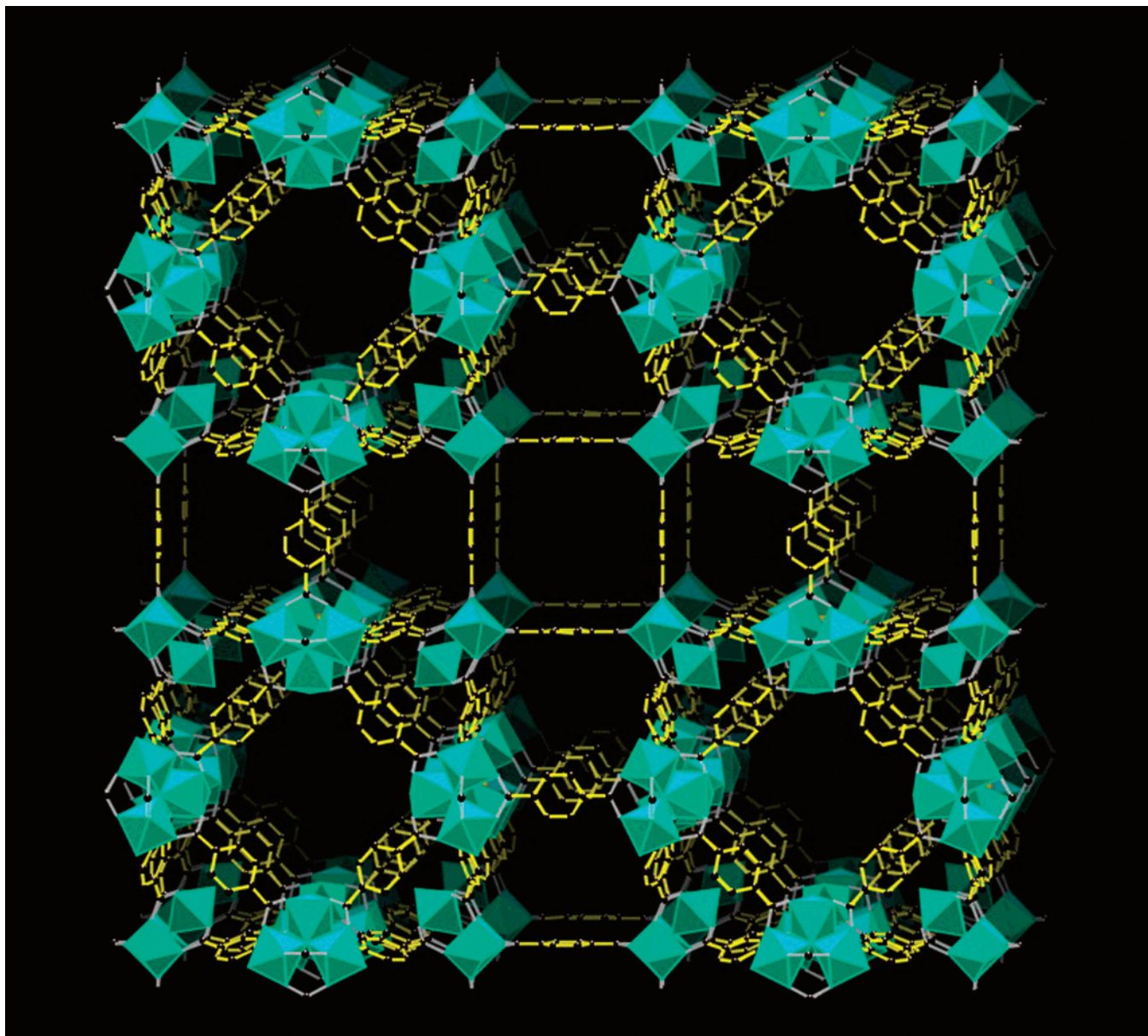


FIGURE 4. An unknown topology resulting from the combination of an octahedral trimer with terephthalic acid.

supertetrahedra, has only pentagonal windows (free openings $\sim 4.8 \text{ \AA} \times 5.8 \text{ \AA}$ for BTC and $\sim 12.5 \text{ \AA} \times 12.5 \text{ \AA}$ for BDC) and an internal *free* diameter of $\sim 25 \text{ \AA}$ ($\sim 30 \text{ \AA}$ with BDC). The connection of the pentagonododecahedral cages creates larger cavities, limited this time by 28 supertetrahedra with 12 pentagonal and 4 hexagonal windows (free aperture $\sim 8.6 \text{ \AA} \times 8.6 \text{ \AA}$ (BTC) and $\sim 16.3 \text{ \AA} \times 16.3 \text{ \AA}$ (BDC)). The internal *free* diameter becomes close to 29 (BTC) and 34 \AA (BDC). It is another breakthrough of our method. Indeed, in inorganic chemistry, such dimensions were only reached with mesoporous solids with amorphous walls. Thus, MIL-100 provides the first example of a porous solid with crystallized walls with a unique hierarchical system of three types of cages of different dimensions ranging from nano- to mesoporosity. The coexistence of the latter two is illustrated by the gaseous N_2 sorption isotherms on the fully evacuated samples, which are between type I and IV. This leads to

pore volumes near 1.16 (BTC) and 1.96 cm^3/g (BDC) and apparent Langmuir surface area of 3100(40) and 5650(40) m^2/g , respectively, which constitutes a new record.⁴⁶ Interestingly, the arrangement of the supertetrahedra in MIL-100 and MIL-101 present (Figure 5f) the same topology as a well-known zeolite (MTN-type),⁴⁷ the supertetrahedra replacing the single tetrahedra in the latter. It therefore illustrates once more the “scale chemistry” concept.²⁰

Computer simulations found two polymorphs of this new structure type with the same relative “energy” cost. One is cubic ($Pm\bar{3}n$) (volume = 64 500 \AA^3) and is the upper analogue of another zeolite, MEP. The other, a hexagonal ($P6_3/mmc$) one (volume 23 600 \AA^3), has no known equivalent in denser structures. They are all built from the same supertetrahedra. In all of them, the pentagonododecahedra are present. Only their connection in 3D space is different and leads to large cages with 26

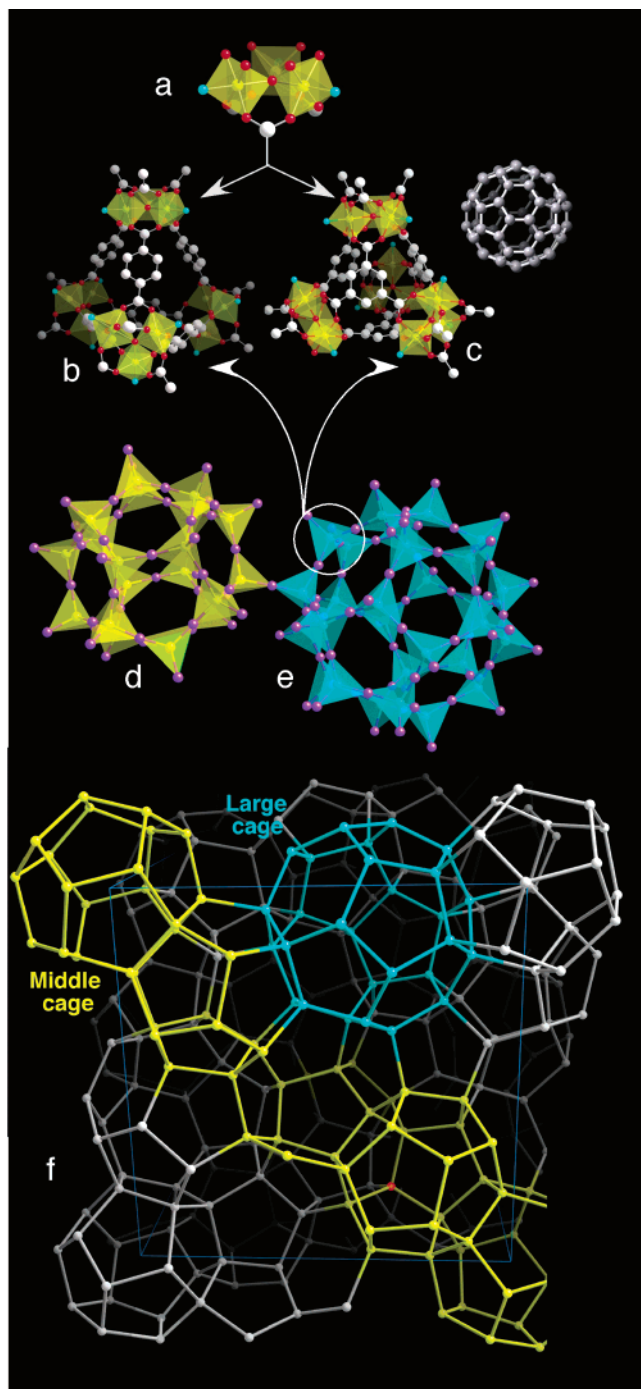


FIGURE 5. The 3D structures of MIL-100 and MIL-101. The inorganic octahedral trimeric units (a) link to BTC in MIL-100 (b) or to BTC in MIL-101 (c) to form supertetrahedra (ST). These supertetrahedra are corner-linked and build up two types of cages: yellow (d) with 20 ST and blue (e) with 28 ST. Figure 5f gives a polyhedral representation of these cages, the vertices corresponding to the centers of ST.

vertices instead of 28 in the cubic polymorph, while the hexagonal one exhibits the same large cages as MIL-100 and MIL-101.

Expected and Unforeseen Limits. In many aspects, this new method pushes forward the limits of what was thought to be possible. First, as soon as the chemistry is mastered for a given type of inorganic SBU, the combination of this chemistry and simulation avoids the recourse

to single crystals, which is always a difficult step before reaching the crystal structure. It is the first limit that has been suppressed. This represents a useful gap because it is sure that many solids previously isolated by several groups were abandoned owing to the lack of single crystals and the complexity of their X-ray powder patterns. For the first time in the realm of MOFs, our method turns out to be a tangible route toward structure solution in *the direct space*. With such a method at hand, formerly untractable structural problems using conventional reciprocal space methods become now feasible in the direct space, starting with minimal knowledge such as the metal/organic ratio or predefined hybrid SBUs.

This challenging area is of crucial interest when very large cell dimensions are involved, pushing the use of diffraction techniques to their limits. Indeed, even with the recent developments of powder diffraction and of ab initio determinations of crystal structures, these new tools have limits. It was recently shown⁴⁸ that, with the use of synchrotron radiation powder diffraction data, a minimal middle height width (FWMH of $0.02^\circ(2\theta)$) for the Bragg peaks allows the ab initio resolution of a centric *fcc* structure only if its cell volume is less than $288\,000\text{ \AA}^3$. This clearly shows that all the available conventional X-ray diffraction methods would have failed for MIL-100 and MIL-101 ($380\,000$ and $706\,000\text{ \AA}^3$) in the absence of good single crystals.

With such cell volumes, which are typically in the same range as protein molecules, another limit is on the way to being reached when other solids with larger volumes will be prepared: the resolution power of the diffraction techniques. This was not foreseen when we created the method. Indeed, as soon as the cell parameters increase, the spots in the electron microscopy diffraction patterns become closer and closer. It is well illustrated by those of MIL-101, which prove first the excellent crystallinity of this solid but also the very short distance between diffraction peaks, evidenced by comparison with the extent of the direct beam. The same can be imagined for synchrotron data. MIL-101 is a favorable case because it is cubic, which rules out any overlap for the Bragg peaks, but it can be anticipated that when the symmetry decreases for giant cells, the complexity of the pattern will be so high that the deconvolution of the peaks could become untractable unless larger wavelengths are used.

Another limitation concerns computing time. With very large cells (typically $2\,000\,000\text{ \AA}^3$), the CPU time exceeds 24 h using an Octane SGI R12000 workstation operating at 300 MHz. The prediction in reasonable times of larger cells will need computers with higher performances. And chemically? It is the only domain for which it is impossible to imagine limits to the reactivity.

As a conclusion, one could say that our results represent valuable “design”. We do not think so because in design, one must first *imagine* something and *realize* it after. In our approach, the first step is not imagination (which means a voluntary creative act), but the result of a predictive approach. For this reason, we prefer to suggest

the label of simulation-assisted chemical structures (SACS) for the solids to be described when using our method in the future.

Finally, some colleagues often cite the provocative sentence of John Maddox: “One of the continuous scandals in the physical sciences is that it remains in general impossible to predict the structure of even the simplest crystalline solids from the knowledge of their chemical composition”. We can now reply: “It is done for MOFs, Mr Maddox! And, as a bonus, we give you the polymorphs!”

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