

# Microporous Solids: From Organically Templated Inorganic Skeletons to Hybrid Frameworks...Ecumenism in Chemistry

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This short review describes the evolution of the nature of microporous solids and the related concepts that were at the origin of this evolution. The paper begins with the different families of classical organically templated inorganic porous solids, their parameters of synthesis, the mechanisms of formation, their consequences, and their limits. From the latter, the concept of hybrid organic–inorganic frameworks is introduced as well as their tentative classification according to the decrease of the dimensionality of the inorganic subnetwork. The last part of the paper is devoted to the new trends in the field: the creation of very large pores, their design from topological considerations, and the introduction of computational methods.

## Introduction

At the end of the last century, solid state chemistry and materials science provided fascinating solids that gave rise to significant breakthroughs in the History of Science: high  $T_c$  superconductors<sup>1,2</sup> in the 1980s and fullerenes<sup>3</sup> and giant magnetoresistive materials<sup>4</sup> in the 1990s, all products that influence or will influence the economy of developed countries during the new millennium. Besides these new important families, the domain of porous solids,<sup>5</sup> which concerns chemicals, petrochemicals, oil refining, fine chemicals, pharmaceutical, catalysis, separation, and environmental technologies,<sup>6,7</sup> is historically much older and economically important already (in the mid-1990s, they represented in the world a turnover of 1000 billions dollars per year and ca. 25% of the Gross Domestic Product<sup>8</sup>).

This domain currently knows an explosion<sup>5</sup> owing to the new approaches to obtain porous solids that have been described during the last 5 years. It was first represented by zeolites, alumino- and gallophosphates. The framework was inorganic and the organic moieties, within the pores, acted as templates that, by leaving the structure by heating, generated the porosity; except in a few systems, the mechanism of their formation was poorly known and a real design of an inorganic open framework was difficult to reach, even if new trends improve the possibilities. The recent discovery of hybrid porous solids in which the framework is built up from both organic and inorganic moieties, strongly connected by covalent bonds, gives a new dimension to the domain. Indeed, the introduction of organic components, their incremental possibilities allowing for instance a modulation of the dimensions of the pores as a function of the length and the shape of the organic chains, renders the walls of the pores more hydrophobic and, therefore, weaken the host–guest interactions and give immediately accessible porosities. This paper will show the evolution from purely inorganic skeletons and the corresponding state of the art to the hybrid frameworks and the world that they open for obtaining a real design

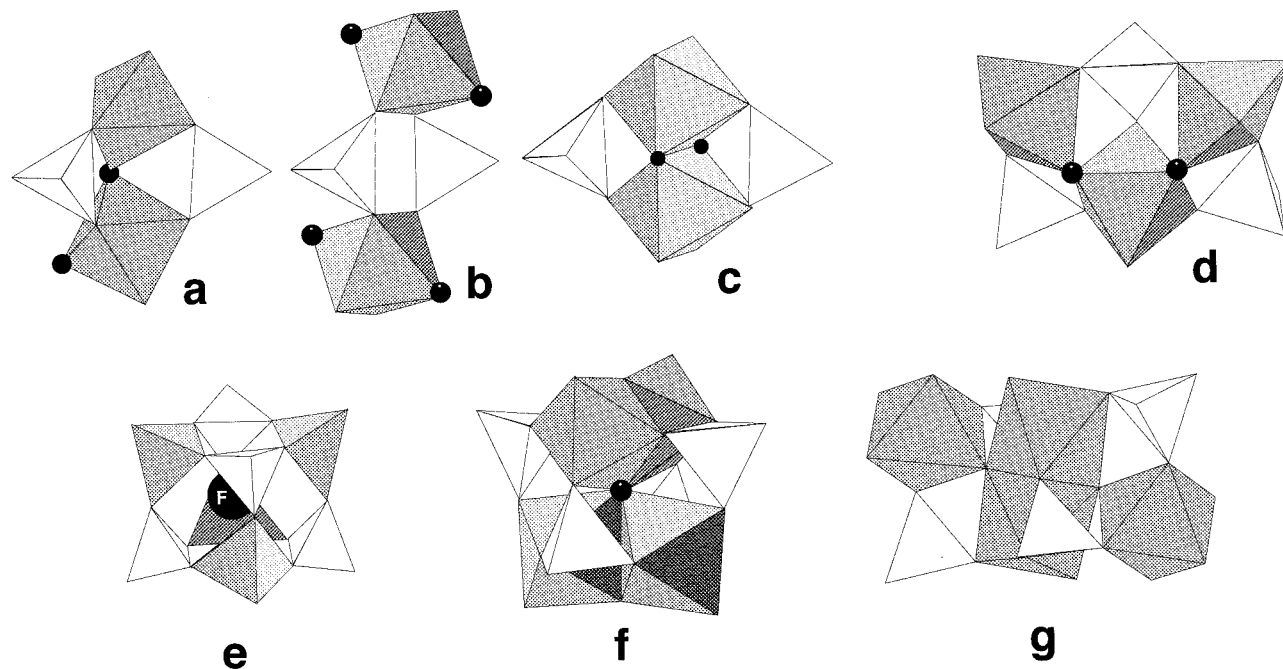
of porous solids, compounds which must already be considered as a continuum between inorganic and organic chemistry.

This review will be strictly limited to microporous solids (pore diameter < 20  ) and will not discuss mesophases with pore sizes in the 20–100-  range<sup>9,10</sup> for which dedicated literature exists. Finally, for the sake of clarity, we have adopted in the text a restricted definition to the term “hybrid”, which usually concerns a much larger class of solids. In the following, despite the fact that the synthesis of all the porous solids requires organic and inorganic moieties, we shall speak about hybrid solids only when the walls of the porous compounds will contain both of these species. Otherwise, when the organic part is located within the pores, the term “organically templated porous solids” will be used.

## Organically Templated Inorganic Porous Solids

**The Different Families.**<sup>5</sup> The concept of porous solids originates from the discovery by Cr nstedt,<sup>11</sup> during the XVIIIth century, of the zeolitic properties of mineral stilbite. Many natural zeolites were discovered later, but the importance of this family increased when chemists were able to synthesize them. The first success was due to Sainte Claire Deville in 1862<sup>12</sup> and most of the syntheses required organic molecules as templates. Today,  $\approx 100$  different types of zeolites are known.<sup>13</sup>

Zeolites (from the greek *zein*, to boil, and *lithos*, stone) are hydrated alkaline or alkaline earth aluminosilicates with the general formula  $M^{n+}_{x/n}[(AlO_2)_x(SiO_2)_y]^{x-} \cdot nH_2O$ . Their framework, built from corner-sharing  $TO_4$  tetrahedra ( $T = Al, Si$ ), delimits interconnected tunnels or cages in which water molecules and M ions are inserted. The porosity is provided by the elimination of the water molecules, the framework remaining unaffected. The cavities, usually quantified structurally by the number of polyhedra surrounding the pore, were primitively used for molecular sieves requirements in gas separation and catalytic purposes. A detailed overview of the field of zeolites is given in refs 14–16.



**Figure 1.** Some of the SBU identified in microporous aluminophosphates.

In 1982, Flanigen and co-workers,<sup>17</sup> playing on the similarity  $2\text{Si}^{4+} \leftrightarrow \text{Al}^{3+} + \text{P}^{5+}$ , synthesized microporous aluminophosphates (hereafter noted AIPOs) with structures related to those of zeolites. The structural studies<sup>18,19</sup> showed however a striking difference between the two families. At variance to zeolites, the Al(Ga)POs framework does not contain only connected tetrahedra since Al and Ga polyhedra can adopt 5- and 6-fold coordinations, which change the connectivity of the framework and therefore the shape of the pores. The change in the coordination polyhedra allows also the introduction of small amounts (<10%) of other metals substituted on Al or Ga (MeAPOs, of special interest for catalytic purposes (refs 6 and 7 and references therein)). This discovery induced a tremendous development of novel mixed octahedral–tetrahedral framework oxides where phosphates can be replaced by silicates and/or arsenates, in particular, titano- and other metasilicates (ref 20 and references therein) discovered by Kuznicki.<sup>21</sup>

The fluoride route for the synthesis of microporous solids by Kessler and co-workers in 1986<sup>22</sup> led to the new class of oxyfluorinated porous solids in which two anions participate in the framework and, sometimes, the fluoride ion acts as a template. Besides the well-known mineralizing role of  $\text{F}^-$ , Kessler and Férey's groups<sup>23–25</sup> showed that this ion also participates in the reaction and in the structure for providing new topologies. This method leads to most of the largest micropores known up to now: VSB-1,<sup>26</sup> cloverite,<sup>23</sup> MIL-31,<sup>27</sup> ULM-5,<sup>28</sup> and ULM-16<sup>29</sup> with tunnels limited by 24, 20, 18, 16, and 16 polyhedra, respectively. This method also opened the way to the synthesis of non-oxide inorganic frameworks: porous sulfides<sup>30–34</sup> and nitrides<sup>35</sup> were discovered in the 1990s and, more recently, porous chlorides and fluorides by Martin and co-workers and O'Hare and co-workers, respectively,<sup>36</sup> besides pure porous manganese oxides.<sup>37</sup> That means that, owing to the cationic variations allowed in the frameworks, even with cations with lone pairs such as Sn(II)<sup>38</sup> and Pb(II),<sup>39</sup> more than one-half of the elements of the periodic

table are now involved in the building of inorganic frameworks.

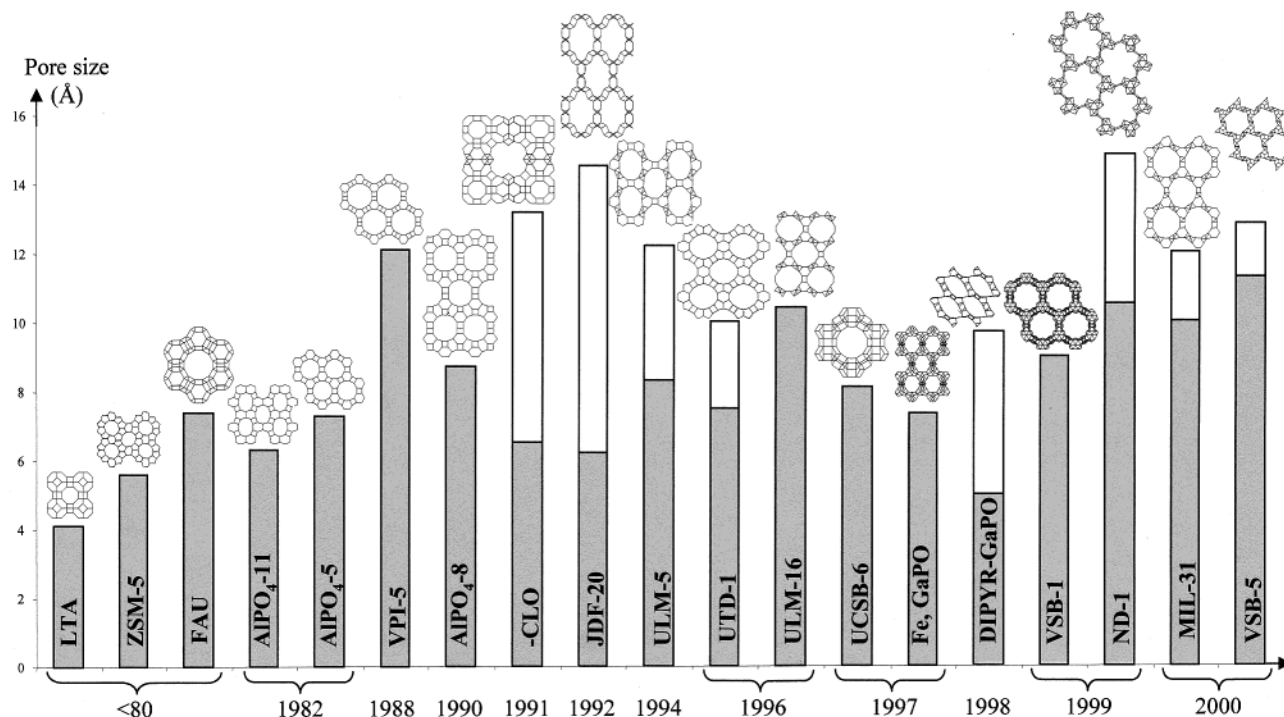
**The Description of Structures.** As stated above, the structures of inorganic frameworks are divided into two different subclasses: the zeotype materials in which all the polyhedra of the wall are exclusively tetrahedra and the mixed tetrahedral–octahedral (or bipyramidal) frameworks.

Primitively devoted to aluminosilicates,<sup>13</sup> zeotypes now include aluminophosphates corresponding to the requirement with the new families of ASU-*n* germanates<sup>40,41</sup> and zeotypic zinc<sup>42–45</sup> and cobalt phosphates<sup>46–48</sup> mainly from the Stucky and C. N. R. Rao groups. The corresponding structures are usually described either by the skeleton of the cationic subnetwork, identified by their Schläfli's symbol, and by the number of cations which surround a window or by 4:2 connected nets, whose exhaustive possibilities of spatial arrangement has been collected by Wells.<sup>49,50</sup> The “openness” of a structure is characterized both by the free aperture of the pores and by the tetrahedral atom density defined as the number of tetrahedral (T) atoms per 1000 Å<sup>3</sup>.

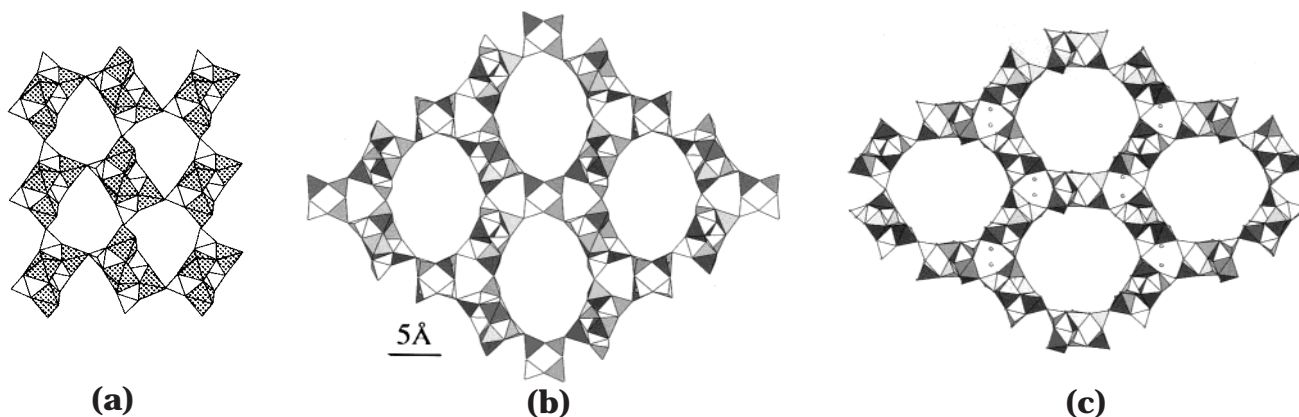
The mixed tetrahedral–octahedral (or bipyramidal) frameworks can also be defined as above, but the description from polyhedra is often preferred. Indeed, the contrast in coordination allows the appearance of oligomeric groups of polyhedra (Figure 1), which allow an easier description of the structures. These oligomers, called SBU-*n* (for “secondary building units” with *n* polyhedra) or tectons, three-dimensionally connected, ensure the framework that can create windows as large as 24-membered rings (Figure 2.).

The importance of the SBU will be illustrated below, in the paragraph concerning mechanisms.

**Synthesis and Pertinent Chemical Parameters.** Most of the syntheses (except porous nitrides) are done in hydrothermal conditions (temperature range 130–200 °C, autogenous pressures 910–30 bar), variable time (from a few minutes to months), which imply a



**Figure 2.** Scale of the dimensions of the pores as a function of time. On the stick, the gray part corresponds to the useful size.



**Figure 3.** Evolution of the size of the tunnels in the ULM (MIL-*n* family as a function of the number *n* of carbons in the templating linear diamines: left ULM-3 ( $3 \leq n \leq 5$ ), middle ULM-5 ( $6 \leq n \leq 8$ ), and right MIL-31 ( $9 \leq n \leq 10$ ).

lowering of the dielectric constant and of the polarizing power of the solvent. The autoclave acts as a “black box” and systematic chemical studies on the systems template- $\text{MO}_n\text{-XO}_p\text{-(HF)-H}_2\text{O}$  ( $M = \text{metal}$ ,  $X = \text{Si, P, Ge, As, etc.}$ ) were needed before any approach to the understanding of the mechanism of formation of the solids was taken. We shall recall here the main conclusions of such systematics obtained with the gallium fluorophosphates ULM-*n*. (See ref 24 and references therein for details and figures.)

pH has a major and complex role: it influences the nature of the phases, the hydration of the amine (at high pH, for example, different 10-membered rings in ULM-3<sup>51</sup> and ULM-4, built from the same SBU-6, but with a hydrated amine for ULM-3 and an anhydrous one for ULM-4), and the nature and the kind of linkage of the polyhedra around the metallic atoms [corner-shared tetrahedra in a basic medium (aluminosilicates), both bipyramids and octahedra at medium pH (metallic phosphates), corner- and edge-shared octahedra at low pH (fluorophosphates)]; moreover—and it will be im-

portant for the future (see last section)—the size of the SBU increases with lowering pH.

Two parameters relative to the nature of the amine are important: the size and shape of the amine (either spherical or linear) and its correlated ability to be protonated. Indeed, there is a relation between their shape and their acidobasic characteristics. Their acidity constants are very different:  $7 < \text{pK}_a < 10$  for aliphatic diamines and  $4 < \text{pK}_a < 6$  for spherical ones. Hence, the volume, the anisotropy of shape, and the charge will influence the structure and the porosity of the solid. Within certain limits, the larger the template, the larger the tunnels, keeping constant the composition of the initial mixture. A good illustration (Figure 3.) is provided with the gallium fluorophosphates templated by linear amines  $\text{NH}_2\text{-(CH}_2)_n\text{-NH}_2$ : 10-membered rings with  $3 \leq n \leq 5$  for ULM-3,<sup>51</sup> 16-membered rings with  $6 \leq n \leq 8$  for ULM-5,<sup>28</sup> and 18-membered rings with  $9 \leq n \leq 10$  for MIL-31.<sup>27</sup>

The role of time and temperature on the nature of the phases and their evolution is often neglected. With



the group of D. O'Hare in Oxford, we recently initiated<sup>52</sup> a systematic study combining chemistry and synchrotron radiation studies for this purpose. We focused on two systems leading to ULM-3 as a final product in hydrothermal conditions, keeping *exactly* constant the composition of the initial mixture and playing only on time and temperature. With 1,3-DAP as the template,  $\text{Ga}(\text{HPO}_4)_2\text{F}$ , DAP,  $2\text{H}_2\text{O}$  is formed at 300 K after 1 week, and its dehydrated form appears either by dehydration at 70 °C in air or when mild hydrothermal conditions are used (120 °C, 3 days). Both phases are one-dimensional with tancoite-type chains containing Ga in octahedral coordination and, as shown by in situ EDXRD, transform at 160 °C in ULM-3 with hydrothermal conditions. EDXRD also shows that the transformation is not direct and implies the dissolution of the chain phase and a solution construction of ULM-3. With 1,4-diaminobutane (DAB), there is only one three-dimensional precursor of ULM-3 below 100 °C, whatever the time. This shows once more the importance of the amine.

**Mechanism of Formation: Hypotheses and Experimental Verification.** Thirty years ago, nothing was known about the mechanism of formation of these solids and about the interactions between organic and inorganic species. This prevented a rational design of microporous compounds, necessary to answer to the increasing demand of the concerned industries.

It is clear that, as soon as results are obtained, there is a tendency to explain the experience by formulating hypotheses that could a posteriori take into account the observations. However, they are only hypotheses with no experimental support for the knowledge of the steps of the reaction. One can only suppose that the hypothesis is true and look at its chemical consequences. In contrast, reaction steps can only be analyzed from in situ studies, which have only been achieved recently, after strong methodology improvements.

For zeolites, two contradictory hypotheses for the crystallization were initially proposed: the first<sup>53</sup> supposed the reorganization of the initial gel and implied a diffusion of ionic species in the solid phases; in the second,<sup>54,55</sup> the diffusion occurs in the liquid phase, the crystallization occurs after a progressive dissolution of the gel, and the dissolved species would aggregate around the organic molecule (template) to give the final solid. The role of the organic part (often an amine) also remains mysterious. If the above hypotheses were true, one amine would lead specifically to one structural type, which is not verified. Davis and Lobo proposed then two different roles of the template according to the flexibility and the geometry of the pores.<sup>56</sup> If the structure is flexible, the template acts only as a space-filling agent; on the other hand, when the shape of the template and the framework are correlated, the template is said to be structure-directing.

Much postulation of reaction mechanism has taken place for metallophosphates. Ozin and co-workers<sup>57</sup> proposed a model for the formation of microporous aluminophosphates in which the reactive building block would be a linear aluminophosphate chain whose components may reassemble through hydrolysis–condensation reactions in solution to precipitate two- and three-dimensional networks. Each step of their hypothesis

requires only the breaking and the creation of a few bonds, but the coordination of aluminum remains tetrahedral. However, recent in situ NMR studies<sup>58</sup> on some AlPOs proved that the coordination of Al, which is 6 at room temperature, decreases to 5 in hydrothermal conditions while the pH changes from acidic to neutral. The studies described in ref 52 prove also that there is not sufficient experimental evidence in support of such a hypothesis.

After his systematic study of the chemistry and the structures of the ULM-*n* series in which he observed that all the structures could be described from a few types of SBU (tetramers  $\text{M}_2\text{P}_2$ , hexamers  $\text{M}_3\text{P}_3$ , and octamers  $\text{M}_4\text{P}_4$ ) with always a formal charge of  $-2$ , Férey proposed<sup>24</sup> a reaction scheme governed by the action of the amine and based on the charge density matching between the structure-directing agent (amine) and the inorganic oligomeric building species (whose size is determined by the density of charge of the diprotonated amine), which may occur in the solution during the formation of fluorinated phosphates. The ammonium–SBU pairs are neutral and allow the precipitation of the solid whose structure will correspond to the lowest lattice energy satisfying the constraints imposed by the size, shape, and plasticity of the SBU–ammonium association. The amine is therefore the driving force of the reaction: (i) the introduction of a given amine in the reaction medium, owing to its  $\text{pK}_a$ , its form, and its length, experimentally imposes a known charge density in a system in which all the other species are variable; (ii) it will determine the evolution in size and charge of the SBU until the latter reaches a charge density and an electronegativity equal to that of the considered amine; (iii) it is at the origin of the creation of the neutral ammonium–SBU pair, which allows the infinite condensation; (iv) when the pair is formed, the steric effects and the flexibility of the amine fix the adopted structure type.

At the present time, it is the only hypothesis that has reached a beginning of experimental proof. This implied recourse for in situ techniques and very large facilities such as the synchrotron radiation. Such studies are now possible in several domains, owing to the major improvements that occurred simultaneously in methodology and academic science during the past 2 decades.<sup>59</sup> Among them, those concerning in situ liquid and solid NMR,<sup>60</sup> energy-dispersive X-ray diffraction (EDXRD) (ref 61 and references therein), and their combination are of crucial importance for the knowledge of what happens in the “black box” autoclave at different stages of the formation of porous solids. NMR may indicate the prenucleation and nucleation species that exist in the solution before the precipitation, whereas EDXRD provides real time information on the mechanisms and kinetics of crystallization and sometimes chemical knowledge impossible to obtain using conventional ex situ techniques.

A cooperative study with Taulelle and co-workers,<sup>62</sup> performed on  $\text{AlPO}_4\text{-CJ2}$ , ULM-3, and ULM-4 (in which all the atoms of the formula are NMR nuclei), combined ex situ and in situ NMR and followed the evolution of many parameters of the synthesis (including the measurement of the absolute value of the pH in hydrothermal conditions) via the NMR characteristics of the

different nuclei versus temperature and reaction time. In the conditions of reaction, the results clearly show in the solution the existence of reactive species (called prenucleation building units or PNBU) whose structure is very close to the SBU existing in the solid: tetramers  $\text{Al}_2\text{P}_2$  for  $\text{AlPO}_4\text{-CJ2}$  and hexamers  $\text{Al}_3\text{P}_3$  for ULM-3 and -4, the only difference being the exclusive 5-fold coordination of Al in hydrothermal conditions related to the increase of internal pH from acidic to neutral for stabilizing such a coordination. Moreover, the results suggest a crystallization mechanism by dissolution–nucleation–growth for  $\text{AlPO}_4\text{-CJ2}$  and ULM-3 and crystallization via a solid–solid reorganization from an amorphous phase for ULM-4. This existence of small oligomeric units seems to be a general phenomenon in metal phosphate chemistry. Indeed, we recently found, using the same technique, that the formation of *both* micro- and mesoporous titanium(IV) phosphates uses tetrameric units  $\text{Ti}_2\text{P}_2$ .

EDXRD studies, performed with the group of D. O'Hare, concerned ULM-3, -4, and -5.<sup>63</sup> They showed the extremely rapid kinetics of the reaction when  $\text{H}_3\text{-PO}_4$  is used as a reactant (typically achieved after  $\approx 1$  h when usual syntheses describe reaction of several days). The solids crystallize directly from the amorphous reaction mixture, the crystal growth being isotropic. From the fit of the curves using Avrami's equation, the synthesis is a purely diffusion-controlled process, observed for the first time with molecular sieve materials. However, if  $\text{P}_2\text{O}_5$  is the starting product, intermediary phases appear after 5 min of induction, with a maximum yield after 15 min, after which ULM-3 or ULM-5 begin to form with a concomitant decrease of the intermediate. The transformation is much slower than both the initial formation of the intermediate and the formation of ULM-*n* when orthophosphoric acid is used as a starting material, taking over 2 h to go to completion. A likely possibility is the intermediate formation of polyphosphates. This illustrates the unexpected influence of the chemical nature of the reagents on the reaction pathways leading to the porous solid.

Very recently, C. N. R. Rao and co-workers<sup>64</sup> introduced a new and very interesting hypothesis concerning the role of amine phosphates as precursors in the formation of open-framework structures. This method is particularly rich and allowed them to isolate amine phosphates intermediates, their further reaction with metal ions forming open framework structures. Of particular interest is the isolation of 4-membered ring monomers and their transformation into complex porous architectures, in a way very close to what we proposed.

#### Further Developments. Magnetic Porous Solids.

The implications of our hypothesis are numerous: it explains that (i) within experimental conditions suitable for the existence of one type of SBU, large diamines lead to lamellar solids, the sheets being built up from the connection of the expected SBU;<sup>65</sup> (ii) with a proper choice of the characters of the amine template, it may be possible to synthesize "tailor-made" solids as for 16-membered ring ULM-16,<sup>66</sup> which used two amines, one for structure-directing purposes and the other, unreactive, for adjusting the pH in a range suitable for SBU-6 oligomers; (iii) the hypothesis is in agreement with the existence of porous solids containing transition metal

ions instead of aluminum and gallium and able to lead to *significant magnetic properties*. Before 1996, only molybdenum and vanadium phosphates were described, but with magnetic ordering temperatures close to 4 K (ref 67 and references therein).

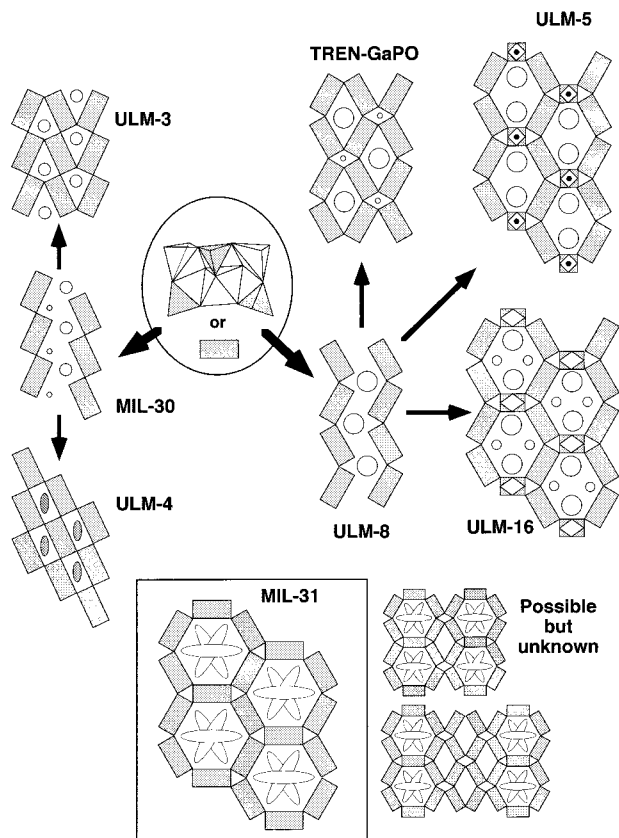
Cavellec et al. (see ref 68 for a review) discovered in 1996 the first series of porous iron(III) fluorophosphates. Most of them are antiferromagnets with magnetic ordering temperatures in the range 10–40 K. These temperatures are relatively high for iron clusters linked by phosphate groups and indicate strong magnetic interactions. Further, Lii and Haushalter groups evidenced oxyphosphates with various SBUs in the structure.<sup>69</sup> Primitively devoted to trivalent ions, this opened the way for intense research on magnetic porous solids, containing either mixed or single valence for the transition metal. The already cited zeotypic cobalt(II) phosphates are involved, in addition to phosphates containing vanadium, titanium, and nickel. With the latter appeared the very promising VSB-*n* family (Versailles-Santa Barbara-*n*). For instance, VSB-1,<sup>26</sup> which was the first microporous solid with 24-membered ring tunnels, is simultaneously porous, magnetic, and an ion exchanger, like the unpublished VSB-5, which is also a fantastic basic catalyst. In this domain (for which, as will be seen below, hybrid solids are concerned), the aim is now to create ferro- and ferrimagnetic compounds with high performances, which implies either a single cation in a mixed valence state or two different cations. MIL-21,<sup>70</sup> a fluorophosphate containing both Fe(III) and V(III), is the first porous ferrimagnet isolated so far.

After this tremendous progress, it seems that there is currently a lack of breakthroughs in the field of organically templated inorganic skeletons, even if one can observe huge variations on the nature of the templates or of the cations and polyanions necessary to build the structures. The SBU concept has proved its strength and, now, variations on the connections between known SBU is currently in progress (Figure 4.). But, even if so many attempts were performed, my opinion is that an intrinsic limit exists for this method.

#### The Limits of the Inorganic Route: An Open Window

The increase in the knowledge of the mechanism of formation simultaneously shows the limits of this method for obtaining "tailor-made" microporous compounds. Indeed, the amine, the driving force for the synthesis, is also the major limiting factor. Its charge induces strong electrostatic interactions with the framework and makes difficult its extraction after the synthesis. Its charge density, which controls the extent of the oligomeric condensation of the SBU, is not so variable and gives rise to limited sizes for these oligomers, apparently limited to eight polyhedra. The ratio between the sizes of the SBU and the amine in the neutral pair limits also the possibilities of connection for having three-dimensional networks. This approach, suitable for having pores in the range say 10–15 Å, restricts the possibilities for easy modulation of the porosity.

The nature and size of phosphates, and more generally of tetrahedral polyanions, is another handicap. Within the SBU, they act as a chelating agent toward

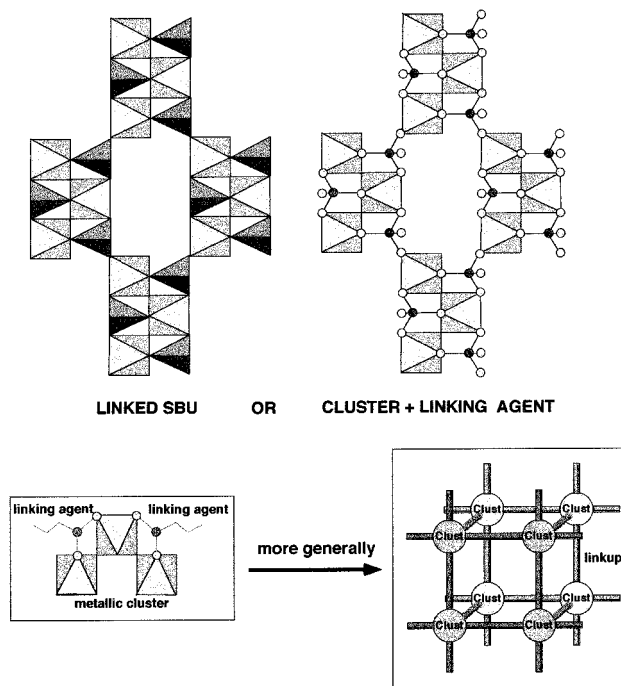


**Figure 4.** Some structures built from the same SBU-6 with different connections and dimensionalities.

the metallic ions and share their oxygens at least with three cations to ensure the three-dimensional network. However, this handicap can be overcome if the SBU are considered as assemblies of metallic clusters linked by chelating agents (Figure 5). Therefore, phosphates can be substituted by modifiable chelates. Alberti and Clearfield (ref 71 and references therein) showed for instance in the early 1970s that phosphonates could replace phosphates in two-dimensional compounds to increase the distance between the layers. That meant that it was possible to create new porous solids by an appropriate choice of both organic and inorganic species for the creation of the framework (my restricted definition for hybrids; see Introduction), the organic part providing an infinite flexibility owing to its richness and therefore an infinity of possible open frameworks. In this way, the past 10 years represent a unique crossroad for chemists of different origins, what I called the “ $\chi$ ”ing in a recent paper.<sup>94</sup>

### The Hybrid Frameworks

It is funny to see once more that the same ideas arise at the same time from several places in the world, even if the ways of thinking that lead to these concepts are completely different. Whereas we developed our strategy based on the creation of phosphate-free hybrid solids by the use of linear diphosphonates and dicarboxylates, Rao and Cheetham et al. discovered the porous oxalato-phosphates, Zubietta described the MOXI-*n* family, Yaghi paved the way for modular porous solids, and a lot of chemists (the name of some leading pioneers will

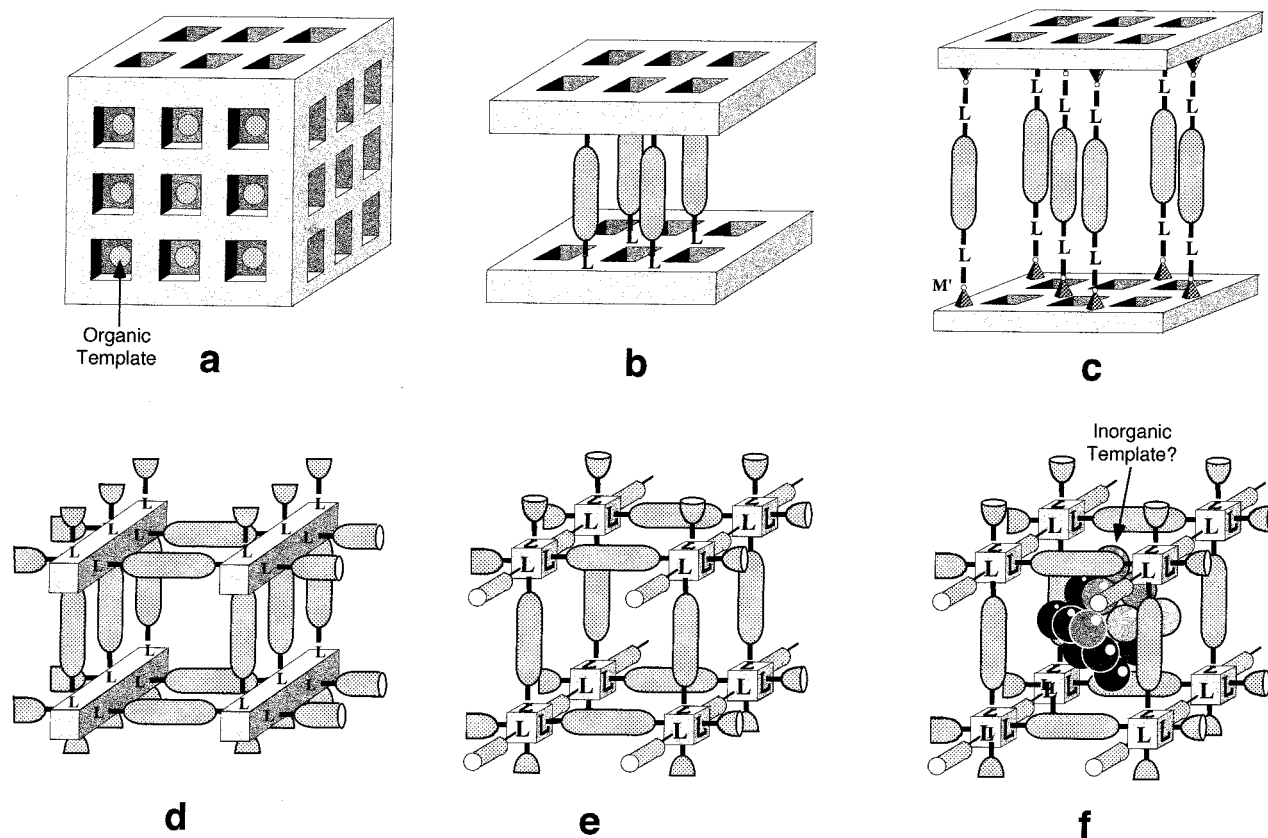


**Figure 5.** Evolution of the description of the porous solids from an assembly of SBU to a framework of clusters linked by organic chelating species.

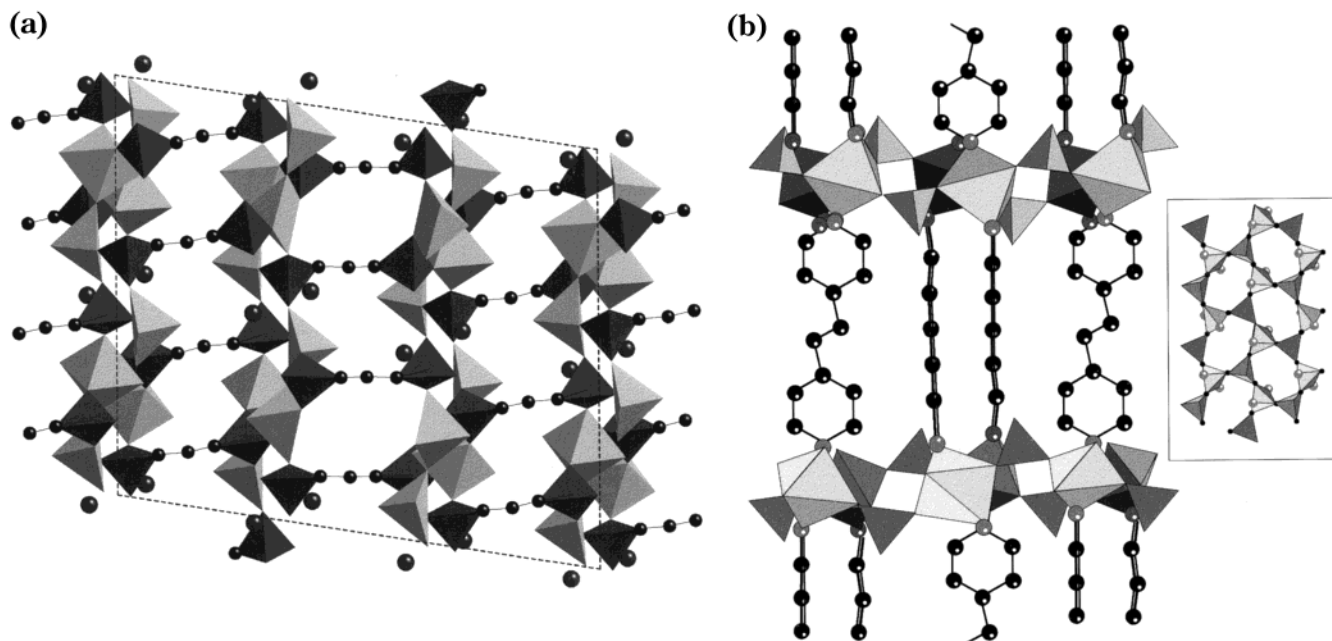
appear below) with either inorganic, coordination chemistry, or even organic cultures came to the field of porous solids. This leads to an explosion of results and a tremendous number of papers and it is rather difficult to classify the results of such “boiling” activity! Looking at the connectivity between inorganic and organic parts in many recently published papers, I am tempted to propose a classification taking into account the decrease of the dimensionality of the inorganic network. Indeed, starting from the organically templated inorganic frameworks (Figure 6a), organic moieties can ensure pillaring between inorganic layers (Figure 6b,c), can act as linkers between inorganic chains (Figure 6d), or arrange (Figure 6e) around zero-dimensional clusters (taken in a general sense for this classification: the cluster can contain several or one cation; if there is no metal, the porous solid is purely organic and the organic parts are linked via hydrogen bonds). Figure 6f relates to a new family of coordination polymers in which oxide clusters reside in the cavities of the hybrid framework. The rest of this section will describe some outstanding examples corresponding to each case of Figure 6. It is clear that my choice is somewhat subjective and I apologize in advance to the colleagues who, despite the quality of their work, are not cited here, but I am sure they are referenced in the leading papers, which are listed at the end of the paper.

**Pillared Inorganic Layers.** The simplest example for the illustration of Figure 6b is provided by MIL-7,<sup>72</sup> a vanadyl propyl diphosphonate (Figure 7a). The carbon chain between the two terminal phosphonic groups acts as linkers between V–P–O layers. Besides, two series are interesting: ferrimagnetic cobalt(II)<sup>73</sup> or some rare earth<sup>74</sup> carboxylates in which the perforated layers of edge-sharing octahedra, with windows delimited by 10, 12, or even 15 polyhedra, are connected by glutarate or succinate groups.





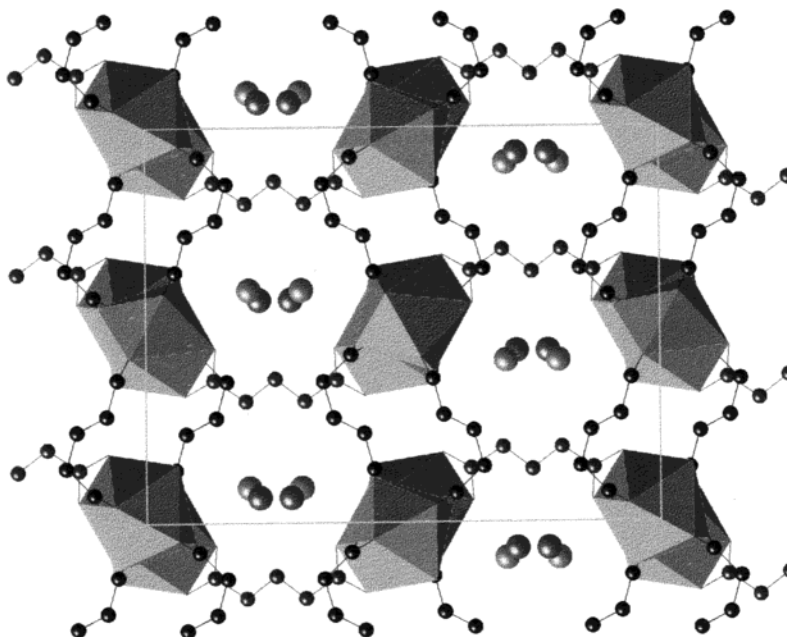
**Figure 6.** Evolution of the dimensionality of the inorganic subnetwork in hybrid microporous solids. (a) 3D in the classical organically templated inorganic frameworks; (b) 2D, with inorganic layers built from one type of cation; (c) 2D, with inorganic layers built from two types of cation, the secondary metal  $M'$ , chosen for its ability to give donor groups attachments; (d) 1D, the grafting of the organics (identical or different) occurring in two directions; (e) 0D with clusters, linked together in the three directions by the ligating species (as mentioned in the text, cluster is taken in its general sense; see text above); (f) coordination polymers including inorganic cluster oxides.



**Figure 7.** (a) (100) projection of the structure of MIL-7.<sup>72</sup> Propyl diphosphonates are represented in dark gray and vanadium square pyramids in light gray. The spheres are water molecules. (b) Structure of MOXI-1 (from ref 75); the tetrahedra are MOO<sub>4</sub>; the copper atoms are in bipyramidal 5-fold coordination CuO<sub>3</sub>N<sub>2</sub>. The circles on these pyramids are the nitrogen atoms coming from dpe.

More general is the MOXI- $n$  family,<sup>75</sup> which corresponds to Figure 6c. Zubietta and co-workers described a very large family based on bimetallic molybdenum

oxides (the other metal is often copper) in which the organic component is introduced as a ligand to the secondary metal site. This strategy is nicely formulated



**Figure 8.** Structure of porous praseodymium glutarate. The glutarates ensure the connection between inorganic chains in two dimensions.

by Zubietta and co-workers: “The overall structure reflects the coordination preferences of the secondary metal site, which are reflected in polyhedral type adopted, donor group attachments and degree of aggregation into oligomeric units, and the geometric constraints of the ligand. The emphasis lies in the design of the ligands and the coordination preferences of the secondary metal site to provide defined structural subunits for fashioning the oxide structure”. Then, the organic ligands (mainly *n*-nitrogen complexes), through the directivity of the covalent bonds, their geometry, and coordination preferences impose the topology and the dimensionality of the resulting network. In these solids, the pores are either empty or filled by water and/or solvent molecules. The structure of MOXI-1 or [Cu(dpe)-(MoO<sub>4</sub>)] provides a nice example of these series. The secondary metal is Cu(II), in a trigonal pyramidal coordination {CuN<sub>2</sub>O<sub>3</sub>}, trans-linked to two (4,4'-bpe) to form {Cu(4,4'-bpe)}<sub>*n*</sub><sup>2*n*-</sup> chains, the three oxygen of the copper coordination being shared with molybdate ions to build up the inorganic layer (Figure 7b).

**Inorganic Chains.** This case, corresponding to Figure 6d, is rather scarce. Our group found some examples of this type<sup>76</sup> in the family of rare earth dicarboxylates and carboxyphosphonates. The most striking example concerns rare earth succinates and glutarates (Figure 8), which ligate chains of trans edge-linked RE polyhedra in 9-fold coordination. The water molecules located in the channels are zeolitic, and the dehydration–rehydration process can be followed by RE spectroscopy.

**Clusters.** This is the domain where the metal–organic chemists gave an outstanding contribution since the beginning of the 1990s, and I take the opportunity to recall the names of some pioneers of the domain in ref 77. Recently, excellent reviews have been published in this field.<sup>78</sup>

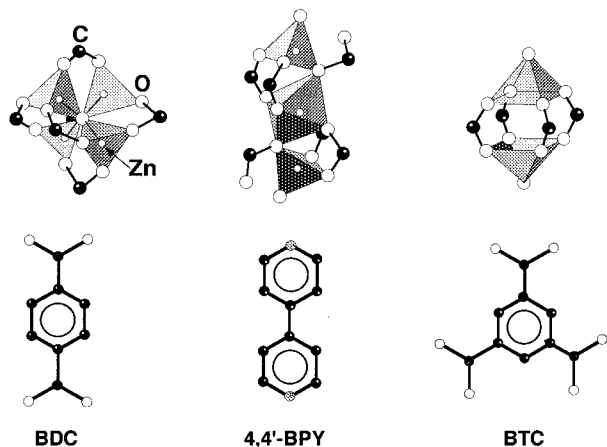
The assets of this community concern the knowledge of assembling a great diversity of inorganic clusters, coordination complexes, and organic molecules into

motifs linked together either by strong metal–ligand bonding, hydrogen bonds, or  $\pi$ – $\pi$  interactions. The stability in the solution and the possibility of functionalization of these moieties and the variability of the lengths of the organic chains a priori provide an infinite number of tools for obtaining three-dimensional assemblies with dimensions of pores much larger than those observed with pure inorganic walls; therefore, they are potentially important candidates for a new generation of porous solids, called according to different authors coordination polymers, modular porous solids, or as in this paper hybrids.

However, some difficulties had to be overcome before any mastery of synthesis could be obtained: (i) a real design is never obvious; (ii) the final products are often poorly crystallized and prevent structure information from being obtained; (iii) their thermal stability is low and many structures collapse in the absence of the guests. As stated by M. J. Zaworotko,<sup>79</sup> many of the “zeolite analogues” of the first generation met these problems, with another intrinsic one: “Nature hates vacuum”. As soon as the dimensions of the cages become a little bit large, two or more independent subnetworks interpenetrate the structure, preventing accessible porosity. The second generation of solids preserved their structural integrity after removal of the guest molecules and allowed reversible exchange of molecules. One can consider that the third generation of hybrid open frameworks began at the end of 1999 with the discovery of MOF-5 by Yaghi and co-workers,<sup>80</sup> which has real advantages over the usual zeotypic materials.

The isolation of this outstanding solid was the result of a strategy elaborated on 5 years before,<sup>77,78</sup> the elegance of which is at the same level as its conceptual simplicity. It consists of associating well-known<sup>81</sup> discrete di-, tri-, or tetranuclear metal carboxylates with multidentate rigid organic building blocks to enhance the rigidity and the stability of the resulting open frameworks. The rigidity of the building blocks is





**Figure 9.** Schematic view of the SBUs used by Yaghi and co-workers for MOF-*n* solids.

ensured by benzenic cycles, the latter giving rise to  $\pi$ - $\pi$  interactions able to render the frameworks interwoven instead of interpenetrated, as will be seen later.

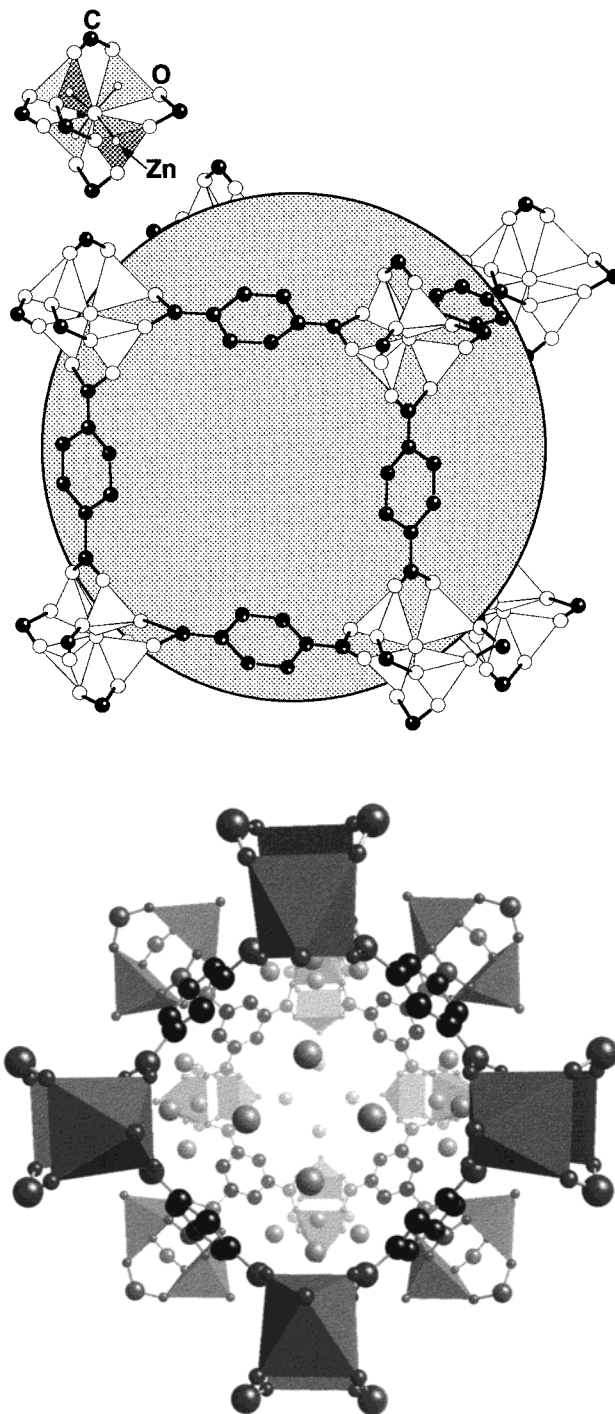
The main building blocks (note that Yaghi and co-workers use now the term SBU!) chosen by Yaghi and co-workers<sup>82</sup> are the dimer “Zn(Cu)<sub>2</sub>(OOC)<sub>4</sub>”, the trimer “Zn<sub>3</sub>(OOC)<sub>6</sub>”, and the tetramer “Zn<sub>4</sub>(OOO)<sub>6</sub>” associated with 1,4-benzene dicarboxylate (BDC), 1,3,5-benzene tricarboxylate (BTC), and 4,4'-bipyridine (Figure 9).

MOF-5 used zinc tetramers associated with BDC. (Figure 10a). The tetramers and BDC are at the vertexes and the edges of the subcell of the large F cubic cell, respectively. The solvent molecules of DMF and chlorobenzene, which occupy the central cavity in the as-synthesized product, can be removed by heating without any structural change of the skeleton. The framework of the desolvated product, stable up to 350 °C, occupies only 20% of the crystal volume (density: 0.59 g·cm<sup>-3</sup>) and leaves a cavity with 18.5-Å free diameter (with no interpenetration) and a surface area of 2900 m<sup>2</sup>·g<sup>-1</sup>. The sorption of nitrogen shows a reversible type I isotherm, as for zeolites. It is noteworthy that the structural topology of MOF-5 was encountered before in a zinc phosphate.<sup>83</sup>

Using a different association (copper dimer and BTC) of the SBUs of Figure 9, Williams and co-workers<sup>84</sup> synthesized HKUST-1, a hydrated copper trimesate with a little bit lower performances ( $d = 1.22$  g·cm<sup>-3</sup>, surface area of 920 m<sup>2</sup>·g<sup>-1</sup>, 14-Å free diameter). The cage (Figure 10b) contains exclusively water molecules, which evolve the structure at 100 °C.

The metallic (Al, Fe, Co) oxalatophosphates of Huang and Lii<sup>85</sup> and Rao and Natarajan and co-workers<sup>86</sup> enter into this classification as well as the very strange new family of composites cadmium oxalates-alkaline halides in which the clusters are composed of six corner-sharing cadmium trigonal prisms surrounding a chloride anion (ref 86, last two references).

**Isolated Metallic Polyhedra.** It is probably, up to now, the most important family of hybrid open frameworks. The metal serves as a knot between the organic species and a tremendous choice of metals and organic linkers is possible as soon as the latter can ligate the metal. Once more, one finds diphosphonates<sup>87</sup> with a special mention for methylene diphosphonates, which are close to pyrophosphates, rare earth oxalates, and

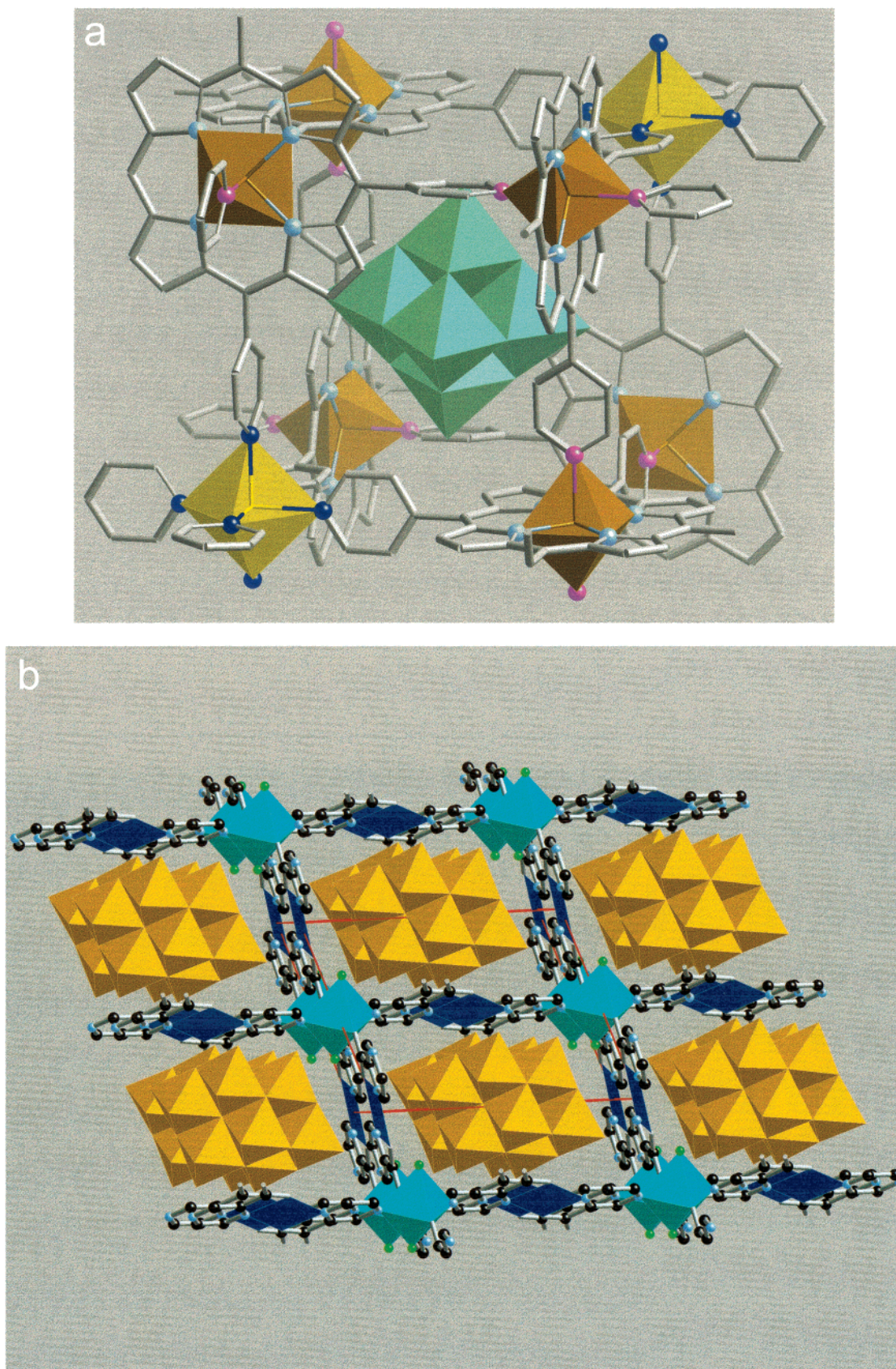


**Figure 10.** Perspective view of (a) the structure of MOF-5 and (b) the cavity in HKUST-1.<sup>84</sup>

dicarboxylates containing one or two cations,<sup>88</sup> organodinitrogen complexes, and so forth. The list of ligands is very long and the reader could consult the special issue<sup>89</sup> dedicated to the design of solids to have an idea of the large number of possibilities that already exist.

In this category, a special case concerns a new family that, in my opinion, is promised brilliant development: hybrid open frameworks with polyanionic species within the pores. The most striking example<sup>90</sup> is given by Zubieta and co-workers and concerns an iron(II)tetrapyridylporphyrine [Fe(tpypor)] including Mo<sub>6</sub>O<sub>19</sub> moieties (Figure 11a). There are two types of iron octahedra in the cationic framework. One resides in the heme pocket;





**Figure 11.** Perspective view of (a) the iron octahedra within the heme pocket of the macrocycle are orange with four nitrogens (pale blue) from the porphyrinic center, the two others (pink) coming from the nitrogen of the pyridyl satellites. The yellow octahedra refer to the arrangement of the macrocycles within the structure, which leads to iron complexed by six nitrogens (dark blue) of the satellites of the macrocycle. The cage inserts the hexameric octahedral species Mo<sub>6</sub>O<sub>19</sub> (in green). (b) Cu<sub>3</sub>(pzc)<sub>4</sub>, V<sub>10</sub>O<sub>28</sub>. Copper atoms are in two types of coordination: octahedral (pale blue) and square planar (deep blue). Iron atoms are yellow and orange and water molecules on the copper octahedron are green.



it is additionally axially coordinated to two adjacent [Fe(tpypor)]. The other is octahedrally coordinated to six pyridyl nitrogen donors. The cubic cages are occupied alternatively by the  $\text{Mo}_6\text{O}_{19}$  moieties and water/solvent molecules. A question arises from this example, if one looks at the evolutions within the different porous families: must  $\text{Mo}_6\text{O}_{19}$  units be considered as the inorganic template of an organic framework or, as stated by Zubietta and co-workers, as a "ship in the bottle" approach to modification of oxide microstructures?

With the same idea, A. J. Jacobson and co-workers discovered very recently a series of copper pirazine carboxylates with copper in square-planar and octahedral coordination,<sup>91</sup> which insert decavanadates ions (Figure 11b).

The final and extreme step of this evolution is of course the lack of inorganic species. Organic synthesis can also lead to microporous solids in which the skeleton is exclusively based on organic species, with the alternation of covalent and hydrogen bonding to ensure the three-dimensional character. A nice example was provided by Endo et al.<sup>92</sup> who created orthogonal anthracene-bis(resorcinol) derivatives, organic analogues of zeolites.

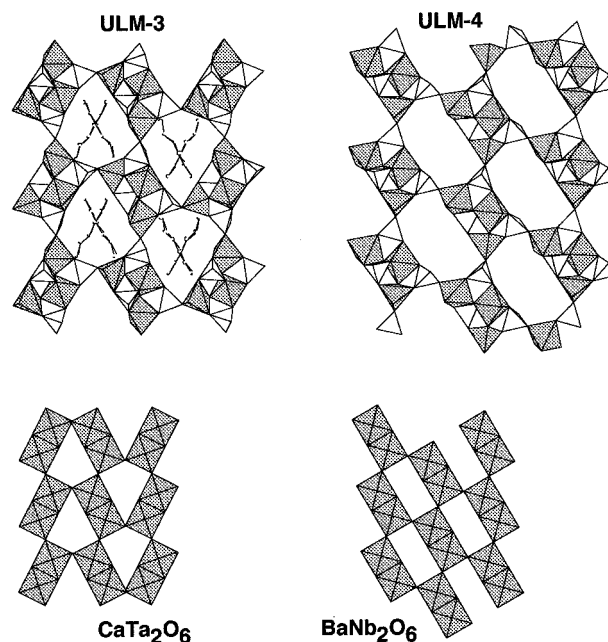
### A New Trend: The Creation of Very Large Pores from Both Methods

Increasing knowledge of the synthesis parameters of porous solids with both pure inorganic or hybrid skeletons opened the way, 2 years ago,<sup>93</sup> to a new challenge, the creation of very large pores maintaining, at variance to mesoporous solids, a strict atomic ordering in the walls. Three approaches are currently selected.

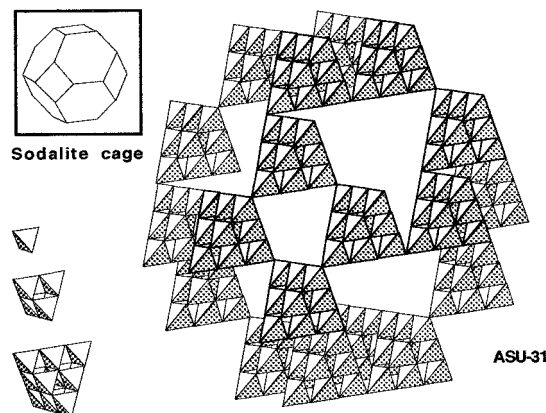
*The scale chemistry concept*,<sup>94</sup> which starts from the idea of a SBU. It was seen above that, within a given system, the size of the SBU increases when the pH decreases. This modulation in size of the SBU can be used to increase the dimensions of the pores, keeping the same topology. The larger the SBU, the larger the pores! I shall illustrate that with three examples among those described in ref 94.

The well-known barium niobate  $\text{BaNb}_2\text{O}_6$  and calcium tantalate  $\text{CaTa}_2\text{O}_6$ , which are built from pairs of edge-shared octahedra as SBUs, have an upper analogue with the structures of ULM-3 and ULM-4,<sup>95,96</sup> 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) (Figure 12).

The most impressive example concerns the sulfides ASU-31 (Figure 13) and ASU-32, recently discovered by Yaghi and co-workers.<sup>97</sup> With other groups, like those of Parise and co-workers,<sup>98</sup> Ozin and co-workers,<sup>99</sup> and Kim and Kanatzidis,<sup>100</sup> they were interested in supertetrahedra. Indeed, starting from structures based on single  $\text{MX}_4$  tetrahedra, other ones are built from assemblies of four corner-shared tetrahedra ( $(\text{Ge}_4\text{Si}_{10})^{4-}$  ions), labeled T2, or 10 corner-shared tetrahedra ( $(\text{In}_{10}\text{S}_{20})^{10-}$  ions), labeled T3. The corresponding SBUs, linked by corners, create three-dimensional solids, either dense or related to the  $\beta$ -cristoballite structure or also built from two interpenetrated subnetworks (see references of the structure types in refs 12 and 97–100). The unique character of ASU-31 and ASU-32 is that the T3



**Figure 12.** Comparison of the size of the vacancies (scale chemistry) between niobates or tantalates and ULM-3 and 4, which exhibit the same topology, but different SBU; one octahedron for the oxides, SBU-6 for the ULM. The structures are at the same scale.



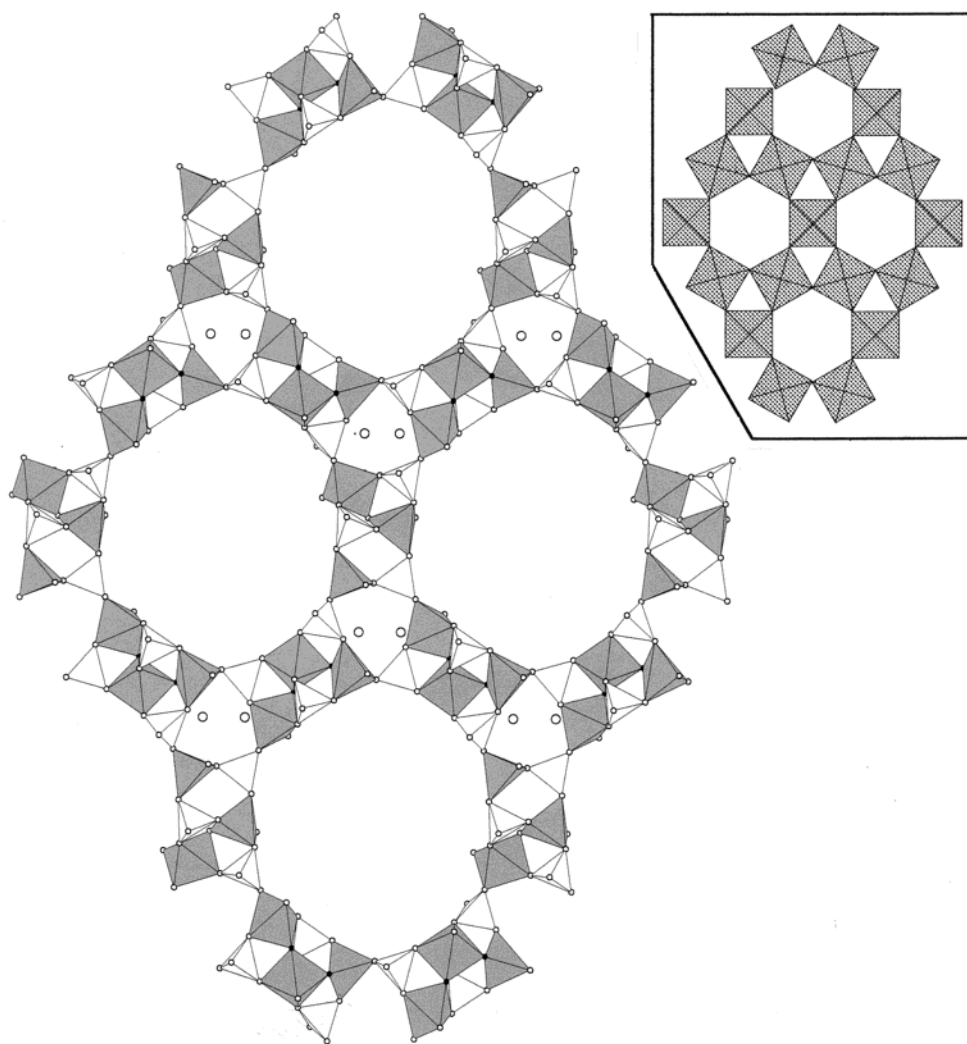
**Figure 13.** Structure of ASU-31, built from supertetrahedra as SBU, which exhibits the sodalite topology.

SBUs 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  $\text{CrB}_4$  net for ASU-32, leaving cage diameters of 25.6 and 17.2 Å, respectively.

The "hexagonal tungsten bronze" structure topology<sup>101</sup> is found (Figure 14) using bricks as different as single octahedra, SBU-6 hexamers (in MIL-31,<sup>102</sup> the mixed tetrahedral-polyhedral analogue of VPI-5,<sup>103</sup> tetramers of edge-sharing octahedra in MIL-16, a porous cobalt succinate,<sup>104</sup> and even cyclodextrins<sup>105</sup> in which the free aperture of the channel becomes more than 36 Å!

*The Müller's three-dimensional connection of very large SBU.* In the past 10 years, A. Müller and co-workers have developed a very original approach concerning the creation of very large polyoxometallic synthons such as big wheels containing up to 248 molybdenum atoms (for the moment!) (ref 106 and references therein). These very large moieties were isolated in the corresponding structures and Müller and





**Figure 14.** Comparison between HTB-FeF<sub>3</sub> (see text) and MIL-31, which both possess the hexagonal tungsten bronze structure topology. The two structures are at the same scale.

co-workers very recently discovered (ref 107 and references therein) a new pathway, comparable to classical inorganic condensation reactions conducive to polycations, which allows the connection of these synthons and therefore generates three-dimensional solids. The first example (Figure 15) concerns the condensation of spherical entities (diameter: 25 Å) containing 72 molybdenum atoms and 30 iron atoms, which leaves free apertures of more than 30 Å. I. Khan (ref 108 and references therein) also developed this strategy with polyoxovanadates.

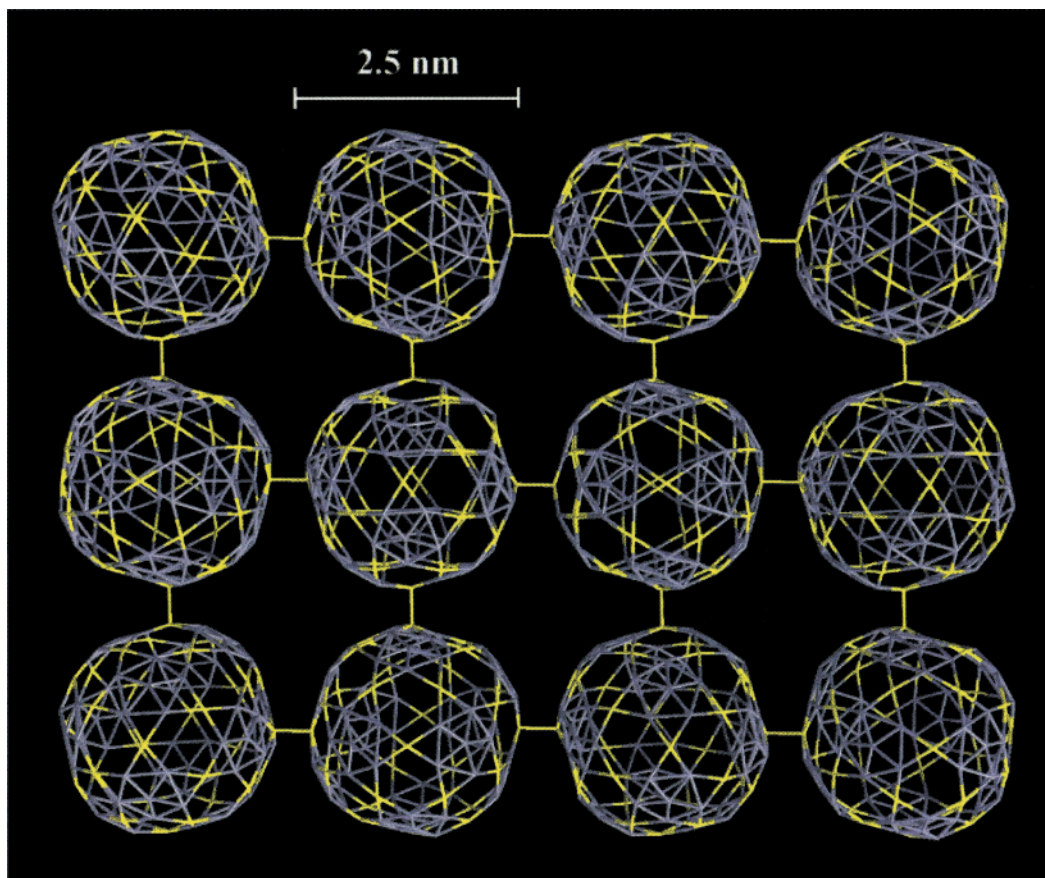
*The building of frameworks for extended solids* is the last approach. It is very recent and will probably influence the community for many years owing to its elegance and generality (refs 109–111 and references therein). In the Special Issue of the Journal of Solid State Chemistry dedicated to the design of solids, O’Keeffe and co-workers paved the way by introducing the geometrical principles of this approach.<sup>110</sup> This is indeed a topological concept in which chemistry occurs only at the end of the process and provides to my opinion the first real tool for design of porous solids.

Behind this concept, there were three requirements: the final framework must (i) be as thermally stable as possible, (ii) avoid or minimize interpenetration, and (iii)

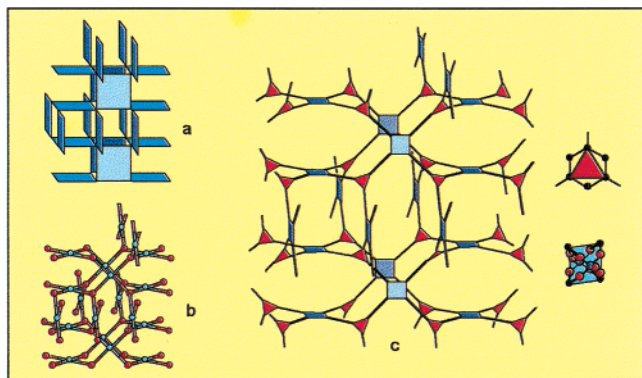
preserve the accessibility of the pores. To fulfill these conditions, O’Keeffe and co-workers fix a priori a topology, choose the tectons able to create this topology, and further imagine a chemistry to reach the goal.

The originality of the concept is to start from very simple structure types, which are illustrated in every textbook and often correspond to thermodynamically stable structures, to describe them in terms of connected nets<sup>49,50</sup> and to decorate (the authors say “augment”) these nets. The decorations are the *topological* SBUs (see below) of the structure and linkers join them. Here, the simple structure is Pt<sub>3</sub>O<sub>4</sub>, a three-dimensional network of corner-shared square planes (Figure 16a) in which oxygens and platinum atoms are 3- and 4-fold coordinated and build a 3,4-connected net (Figure 16b). The decoration replaces Pt by squares and O by triangles and generates the topology of Figure 16c. Squares and triangles are the topological SBU; that is, they represent species whose *connectivity* is here 4 for the squares and 3 for the triangles, whatever their chemical nature.

In the first example described by O’Keeffe and co-workers,<sup>111</sup> the squares are taken up by a binuclear Cu carboxylate moiety and the triangle is formed by 4,4’,4’’-



**Figure 15.** Fe–O–Fe linkage of giant spheres containing each 72 Mo and 30 Fe atoms (with courtesy of A. Müller).



**Figure 16.** The concept of augmented nets illustrated by the decoration of  $\text{Pt}_3\text{O}_4$  structure represented (a) with a framework of corner-sharing square planes (b) as a balls and sticks model showing the 4- and 3-connectivities of Pt and O, respectively. (c) represents the decorated  $\text{Pt}_3\text{O}_4$  structure with Pt replaced by blue squares and O by red triangles attached to each other by linkers. These topological SBUs correspond to the two Cu square pyramids linked by four carboxylates (top right) (for the square) and by 1,3,5 ramified benzene cycles (for the triangle).

benzene-1,3,5-triyl-tribenzoic acid, with three corners of the benzene ring acting as the vertexes of the inner triangle, the linkers being phenyl groups. The risk of interpenetration is lowered because the  $\pi$ - $\pi$  interactions between the benzyl groups renders the two equal sublattices interwoven instead of interpenetrating. This creates accessible pores with a free diameter of about 16 Å and windows with dimensions of  $7 \times 14 \text{ \AA}^2$  after elimination of the solvents that reside in the cavities (corresponding to a surface area of  $1500 \text{ m}^2/\text{g}$ ).

These properties are remarkable, but are not as important as the new strategy described here. In this strategy, specific chemistry is only introduced after having chosen a desired topology and the tectons that may enable it to be formed. Moreover, this approach is general because it is independent of the nature of the reactants. It only depends on the connectivity of the tectons and thus allows every modulation of the chemical nature of the topological SBUs, and every modulation of the linkers, within a given topology. The composition of a given solid is also known before synthesis because the ratio between the different topological SBUs is fixed by the choice of the initial structure type. With the success of such a strategy, the synthesis of hybrid porous solids will never be like it was before.

### Future Developments. Conclusions

In a recent paper,<sup>94</sup> I concluded: “What is impossible?”. I should be tempted to answer “Nothing” when seeing the tremendous creativity of the chemists during these past few years. It is just a problem of time and imagination. Some products and some concepts were unimaginable 2 years ago are now a reality. The family of porous solids now concerns all branches of chemistry, as I tried to show in this paper. This universality allows actions and dreams.

The chemical activity developing now everywhere, with its multiple variations on the nature of solvents, templates, and building blocks (either organic or inorganic), will, I am sure, give many exciting results, helped by the development of automated combinatorial methods.<sup>112</sup> At the opposite end of the spectrum, I think



that the role of computational studies for the design of novel architectures will increase drastically in the not-too-distant future. The first pioneer attempts by Catlow and co-workers,<sup>113</sup> followed by those of Schön and Jansen<sup>114</sup> and our AASBU method of automated assembly of secondary building units<sup>115</sup> are very promising and already allow generation of (beside known ones) unknown porous topologies and adequate templates. This paves the way to an "a posteriori" and designed chemistry that is, in a sense, very close to the last developments of Yaghi and co-workers.<sup>111</sup>

Finally, my dreams concern the physical properties of the porous solids. The recent discovery of new transition metal porous materials open the possibility of making porous frameworks with electronic properties close to that of the dense phases. What exciting applications can be made for porous materials exhibiting NLO phenomena, ferromagnetism, giant magnetoresistance, ferroelectricity, combined ionic/electronic conductivity, or even superconductivity? These properties can come from the framework, but as I suggested in ref 94, why not from the occluded species? It is one of the reasons for which I believe so much in the giant pores mentioned above. Once more, just do it!

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### Glossary

ASU: Arizona State University  
 HKUST: Hong-Kong University of Science and Technology  
 MIL: Materials of Institut Lavoisier  
 MOF: metal-organic frameworks  
 MOXI: molybdenum oxides  
 MU: Mulhouse University  
 ULM: University Le Mans  
 VPI: Virginia Polytechnic Institute  
 VSB: Versailles-Santa Barbara 2

### References

- Michel, C.; Raveau, B. *Rev. Chim. Miner.* **1984**, *21*, 407.
- Bednorz, A.; Müller, Z. *Physik* **1986**, *B64*, 187.
- Kroto, H. *Nature* **1987**, *329*, 529.
- Rao, C. N. R.; Raveau, B. In *Colossal Magneto Resistance, Charge Ordering and Related Properties of Rare Earth Manganese Oxides*; World Scientific: Singapore, 1998.
- Cheetham, A. K.; Férey, G.; Loiseau, T. *Angew. Chem., Int. Ed.* **1999**, *38*, 3268.
- Thomas, J. M. *Philos. Trans. R. Soc. London A* **1990**, *333*, 173; *Chem. Eur. J.* **1997**, *3*, 1557; *Angew. Chem., Int. Ed.* **1999**, *38*, 3588.
- Corma, A. *Chem. Rev.* **1995**, *95*, 559.
- Davis, M. E.; Maxwell, I. E. *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 55.
- Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.
- Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T. *J. Am. Chem. Soc.* **1992**, *114*, 10835. Beck, J. S.; Vartuli, J. C. *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 76.
- Cronstedt, A. F. *Akad. Handl. Stockholm* **1756**, *17*, 120.
- de Sainte Claire Deville, H. *C. R. Acad. Sci.* **1862**, *54*, 324.
- Meier, W. M.; Olson, D. H.; Baerlocher, Ch. *Atlas of Zeolite Structure Types*; Elsevier: Boston, MA, 1996.
- Breck, D. W. *Zeolite molecular sieves: structure, chemistry and use*, J. Wiley and Sons: New York, 1974.
- Venuto, P. *Microporous Mater.* **1994**, *2*, 297.
- Cheetham, A. K.; Inokuchi, H.; Thomas, J. M. *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 55.
- Wilson, S. T.; Lok, B. M.; Messina, C. A.; Cannan, T. R.; Flanigen, E. M. *J. Am. Chem. Soc.* **1982**, *104*, 1146.
- Smith, J. V. *Chem. Rev.* **1988**, *88*, 149.
- Parise, J. B. *Inorg. Chem.* **1985**, *24*, 4312.
- Rocha, J.; Anderson, M. W. *Eur. J. Inorg. Chem.* **2000**, 801.
- Kuznicki, S. M. U.S. Patent 4 853 202, 1989.
- Guth, J. L.; Kessler, H.; Wey, R. *Stud. Surf. Sci. Catal* **1986**, *28*, 121.
- Estermann, M.; McCusker, L.; Baerlocher, C.; Merrouche, A.; Kessler, H. *Nature* **1991**, *352*, 320.
- Férey, G. *J. Fluorine Chem.* **1995**, *72*, 187. Férey, G. *C. R. Acad. Sci. Sér. IIC* **1998**, *1*, 1.
- Férey, G.; Loiseau, T.; Riou, D. In *Advanced inorganic fluorides: synthesis, characterizations and applications*; Nakajima, T., Tressaud, A., Zemva, B., Eds.; Elsevier: New York, 2000; p 209.
- Guillou, N.; Gao, Q.; Nogues, M.; Morris, R.; Hervieu, M.; Férey, G.; Cheetham, A. K. *C. R. Acad. Sci. Sér. IIC* **1999**, *2*, 387.
- Sassoye, C.; Loiseau, T.; Taulelle, F.; Férey, G. *Chem. Commun.* **2000**, 943.
- Loiseau, T.; Riou, D.; Taulelle, F.; Férey, G. In *Zeolites and related microporous materials: State of the art*; Weitkamp, J., Karge, H. G., Pfeiffer, H., Homderich, W., Eds.; Elsevier: New York, 1994; Vol. 84A, p 395.
- Loiseau, T.; Férey, G. *J. Mater. Chem.* **1996**, *6*, 1073.
- Kim, K. W.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1992**, *114*, 4878; *J. Am. Chem. Soc.* **1998**, *120*, 8124.
- Bedard, R. L.; Wilson, S. T.; Vail, L. D.; Bennett, J. M.; Flanigen, E. M. *Stud. Surf. Sci. Catal. A* **1989**, *49*, 375.
- Yaghi, O. M.; Sun, Z.; Richardson, D. A.; Groy, T. L. *J. Am. Chem. Soc.* **1994**, *116*, 807.
- Cahill, C. L.; Ko, Y.; Parise, J. B. *Chem. Mater.* **1998**, *10*, 19 and refs therein.
- Scott, R. W. J.; MacLachlan, M. J.; Ozin, G. A. *Curr. Opin. Solid State Mater. Sci.* **1999**, *4*, 113 and references therein.
- Schnick, W.; Lücke, J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 213. Stock, N.; Irran, E.; Schnick, W. *Chem. Eur. J.* **1998**, *4*, 1822. Lauterbach, R.; Schnick, W. *Solid State Sci.* **2000**, *2*, 463.
- Martin, J. D.; Greenwood, K. B. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2072. Martin, J. D.; Dattelhaum, A. M.; Thornton, T. A.; Sullivan, R. M.; Yang, J.; Peachey, M. T. *Chem. Mater.* **1998**, *10*, 2713. Francis, R. J.; Halasyamani, P. S.; O'Hare, D. *Angew. Chem., Int. Ed.* **1998**, *37*, 2214. *Chem. Mater.* **1998**, *10*, 3131. Walker, S. M.; Halasyamani, P. S.; Allen, S.; O'Hare, D. *J. Am. Chem. Soc.* **1999**, *121*, 10513.
- Brock, S. L.; Duan, N.; Tian, Z. R.; Giraldo, O.; Zhou, H.; Suib, S. L. *Chem. Mater.* **1998**, *10*, 2619.
- Ayyappan, S.; Bu, X.; Cheetham, A. K.; Natarajan, S.; Rao, C. N. R. *Chem. Commun.* **1998**, 218.
- Ayyappan, S.; Diaz de Delgado, G.; Cheetham, A. K.; Férey, G.; Rao, C. N. R. *J. Chem. Soc., Dalton Trans.* **1999**, *17*, 2905.
- Li, H.; Yaghi, O. M. *J. Am. Chem. Soc.* **1998**, *120*, 8567.
- O'Keefe, M.; Yaghi, O. M. *Chem. Eur. J.* **1999**, *5*, 2796.
- Harrison, W. T. A.; Martin, T. E.; Gier, T. E.; Stucky, G. *J. Mater. Chem.* **1992**, *2*, 175.
- Feng, P.; Bu, X.; Stucky, G. D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1745.
- Yang, G. Y.; Sevov, S. C. *J. Am. Chem. Soc.* **1999**, *121*, 8389.
- Chidambaram, D.; Neeraj, S.; Natarajan, S.; Rao, C. N. R. *J. Solid State Chem.* **1999**, *147*, 154. Neeraj, S.; Natarajan, S.; Rao, C. N. R. *Chem. Mater.* **1999**, *23*, 303.
- Cowley, A. R.; Chippindale, A. M. *J. Chem. Soc., Chem. Commun.* **1996**, 673.
- Feng, P.; Bo, X.; Stucky, G. D. *Nature* **1997**, *388*, 735.
- Natarajan, S.; Neeraj, S.; Choudhury, A.; Rao, C. N. R. *Inorg. Chem.* **2000**, *39*, 1426. Natarajan, S.; Neeraj, S.; Rao, C. N. R. *Solid State Sci.* **2000**, *2*, 87.
- Wells, A. F. *Three-Dimensional Nets and Polyhedra*; Wiley: New York, 1977; Further Studies of Three-Dimensional Nets. *Am. Crystallogr. Assoc. Monograph* **1979**, *8*.
- Han, S.; Smith, J. V. *Acta Crystallogr. A* **1999**, *55*, 332.
- Férey, G.; Taulelle, F.; Loiseau, T.; Lacorre, P. *J. Solid State Chem.* **1993**, *105*, 179.
- Walton, R. I.; Millange, F.; Le Bail, A.; Loiseau, T.; Serre, C.; O'Hare, D.; Férey, G. *Chem. Commun.* **2000**, 203. Walton, R. I.; Millange, F.; O'Hare, D.; Loiseau, T.; Paulet, C.; Férey, G. *Chem. Mater.* **2000**, *12*, 1977. Walton, R. I.; Millange, F.; Loiseau, T.; O'Hare, D.; Férey, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 4552.
- Breck, D. W.; Flanigen, E. M. In *Molecular Sieves Soc. Chem. London* **1968**, *47*.
- Barrer, R. M.; Baynham, J. W.; Bultitude, F. W.; Meier, W. M. *J. Chem. Soc.* **1959**, 195.
- Zhdanov, S. P. *Adv. Chem. Ser.* **1971**, *101*, 20.
- Davis, M. E.; Lobo, R. F. *Chem. Mater.* **1992**, *4*, 756.
- Oliver, S.; Kuperman, A.; Ozin, G. A. *Angew. Chem., Int. Ed.* **1998**, *37*, 46.



- (58) Taulelle, F.; Haouas, M.; Gerardin, C.; Estournes, C.; Loiseau, T.; Férey, G. *Colloids Surf. A* **1999**, *158*, 299.
- (59) Cheetham, A. K.; Mellot, C. F. *Chem. Mater.* **1997**, *9*, 2269.
- (60) In-Gerardin, C.; In, M.; Taulelle, F. *J. Chim. Phys.* **1995**, *92*, 1877. Shi, J.; Anderson, M. W.; Carr, S. W. *Chem. Mater.* **1996**, *8*, 369.
- (61) Walton, R. I.; O'Hare, D. *Chem. Commun.* **2000**, 2283.
- (62) Haouas, M.; Gerardin, C.; Taulelle, F.; Estournes, C.; Loiseau, T.; Férey, G. *J. Chim. Phys.* **1998**, *95*, 302. Taulelle, F.; Haouas, M.; Gerardin, C.; Estournes, C.; Loiseau, T.; Férey, G. *Colloids Surf. A* **1999**, *158*, 299. Haouas, M. Thesis, Strasbourg, 1999.
- (63) Francis, R. J.; Price, S. J.; O'Brien, S.; Fogg, A. M.; O'Hare, D.; Loiseau, T.; Férey, G. *Chem. Commun.* **1997**, 521. Francis, R. J.; O'Brien, S.; Fogg, A. M.; Halasyamani, P. S.; O'Hare, D.; Loiseau, T.; Férey, G. *J. Am. Chem. Soc.* **1999**, *121*, 1002. Walton, R. I.; Loiseau, T.; O'Hare, D.; Férey, G. *Chem. Mater.* **1999**, *11*, 3201.
- (64) Neeraj, S.; Natarajan, S.; Rao, C. N. R. *Angew. Chem., Int. Ed.* **1999**, *38*, 3480. Rao, C. N. R.; Natarajan, S.; Neeraj, S. *J. Am. Chem. Soc.* **2000**, *122*, 2810. Rao, C. N. R.; Natarajan, S.; Neeraj, S. *J. Solid State Chem.* **2000**, *152*, 302. Natarajan, S.; Neeraj, S.; Rao, C. N. R. *Solid State Sci.* **2000**, *2*, 87.
- (65) Serpaggi, F.; Loiseau, T.; Riou, D.; Hosseini, M. W.; Férey, G. *Eur. J. Solid State Inorg. Chem.* **1994**, *31*, 583.
- (66) Loiseau, T.; Férey, G. *J. Mater. Chem.* **1996**, *6*, 1073.
- (67) Bonavia, G.; Haushalter, R. C.; Zubieta, J. *J. Solid State Chem.* **1996**, *126*, 292.
- (68) Cavellec, M.; Riou, D.; Férey, G. *Inorg. Chem. Acta* **1999**, *291*, 317 and references therein.
- (69) Lii, H. K.; Huang, Y. F.; Zima, V.; Huang, C. Y.; Lin, H. M.; Jiang, Y. C.; Liao, F. L.; Wang, S. L. *Chem. Mater.* **1998**, *10*, 2599. Debord, R. J.; Reiff, W. M.; Warren, C. J.; Haushalter, R. C.; Zubieta, J. *Chem. Mater.* **1997**, *9*, 1994.
- (70) Riou-Cavellec, M.; Grenèche, J. M.; Férey, G. *J. Solid State Chem.* **1999**, *148*, 150.
- (71) Clearfield, A. *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 268.
- (72) Riou, D.; Baltazar, P. M.; Férey, G. *Solid State Sci.* **2000**, *2*, 127.
- (73) Livage, C.; Egger, C.; Nogues, M.; Férey, G. *J. Mater. Chem.* **1998**, *8*, 2743. Livage, C.; Egger, C.; Férey, G. *Chem. Mater.* **1999**, *11*, 1546.
- (74) Serpaggi, F.; Férey, G. *Microporous Mesoporous Mater.* **1999**, *32*, 311.
- (75) Hagrman, D.; Zubieta, C.; Haushalter, R. C.; Zubieta, J. *Angew. Chem., Int. Ed.* **1997**, *36*, 873. Hagrman, D.; Haushalter, R. C.; Zubieta, J. *Chem. Mater.* **1998**, *10*, 361. Hagrman, D.; Warren, C. J.; Haushalter, R. C.; Seip, C.; O'Connor, C. J.; Rarig, R. S.; Johnson, K. M., III; LaDuca, R. L.; Zubieta, J. *Chem. Mater.* **1998**, *10*, 3294. Hagrman, D.; Sangregorio, C.; O'Connor, C. J.; Zubieta, J. *J. Chem. Soc., Dalton* **1999**, 3707. Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2637. Hagrman, D. E.; Zubieta, J. *J. Solid State Chem.* **2000**, *152*, 141.
- (76) Serpaggi, F.; Férey, G. *J. Mater. Chem.* **1998**, *8*, 2737. Serpaggi, F.; Férey, G. *J. Mater. Chem.* **1998**, *8*, 2749. Serpaggi, F.; Férey, G. *Microporous Mesoporous Mater.* **1999**, *32*, 311. Serpaggi, F.; Férey, G. *Inorg. Chem.* **1999**, *38*, 4741. Serpaggi, F.; Luxbacher, T.; Cheetham, A. K.; Férey, G. *J. Solid State Chem.* **1999**, *145*, 580. Riou-Cavellec, M.; Sanselme, M. F.; Férey, G. *J. Mater. Chem.* **2000**, *10*, 745.
- (77) Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546. Moore, J. S.; Lee, S. *Chem. Ind. (London)* **1994**, *14*, 556. Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151. Yagui, O. M.; Sun, Z.; Richardson, D. A.; Groy, T. L. *J. Am. Chem. Soc.* **1994**, *116*, 807. Zaworotko, M. J. *J. Chem. Soc. Rev.* **1994**, 483. Subramanian, S.; Zaworotko, M. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2127. Venkataraman, D.; Gardner, G. B.; Lee, S.; Moore, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 11600. Yaghi, O. M.; Li, H.; Li, G. *Nature* **1995**, *378*, 703. Yaghi, O. M.; Li, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 207. Yaghi, O. M.; Li, H. *J. Am. Chem. Soc.* **1995**, *117*, 10401. Yaghi, O. M.; Li, H.; Groy, T. L. *J. Am. Chem. Soc.* **1996**, *118*, 9096. Jaitner, P.; Rieker, C.; Wurst, K. *Chem. Commun.* **1997**, 1245.
- (78) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460. Yagui, O. M.; Li, H.; Davis, C.; Richardson, D. A.; Groy, T. L. *Acc. Chem. Res.* **1998**, *31*, 474. Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2637.
- (79) Zaworotko, M. J. *Nature* **1999**, *402*, 242.
- (80) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276.
- (81) Clegg, W.; Little, I. R.; Straugnan, B. P. *J. Chem. Soc. Chem. Commun.* **1985**, 173. Clegg, W.; Little, I. R.; Straugnan, B. P. *J. Chem. Soc. Dalton Trans.* **1986**, 1283. Clegg, W.; Harbron, D. R.; Homan, C. D.; Hunt, P. A.; Little, I. R.; Straugnan, B. P. *Inorg. Chim. Acta* **1991**, *186*, 51.
- (82) Eddaoudi, M.; Li, H.; Reineke, T.; Fehr, M.; Kelley D.; Groy, T. L.; Yaghi, O. M. *Top. Catal.* **1999**, *9*, 105.
- (83) Harrison, W. T. A.; Broach, R. W.; Bedard, R. A.; Gier, T. E.; Bu, X.; Stucky, G. D. *Chem. Mater.* **1996**, *8*, 691.
- (84) Chui, S. S. Y.; Lo, S. M. F.; Charmant, P. H.; Orpen, A. P.; Williams, I. D. *Science* **1999**, *283*, 1148.
- (85) Huang, Y. F.; Lii, K. H. *J. Chem. Soc., Dalton Trans* **1998**, 4085. Lin, H. M.; Lii, H. K.; Jiang, Y. C.; Wang, S. L. *Chem. Mater.* **1999**, *11*, 519.
- (86) Choudhury, A.; Natarajan, S.; Rao, C. N. R. *Chem. Mater.* **1999**, *11*, 2316. Choudhury, A.; Natarajan, S.; Rao, C. N. R. *J. Solid State Chem.* **1999**, *146*, 538. Choudhury, A.; Natarajan, S. *J. Mater. Chem.* **1999**, *9*, 3113. Choudhury, A.; Natarajan, S. *Solid State Sci.* **2000**, *2*, 365. Rao, C. N. R.; Natarajan, S.; Choudhury, A.; Neeraj, S.; Vaidhyanathan, R. *Acta Crystallogr.* **2001**, *B57*, 1. Vaidhyanathan, R.; Neeraj, S.; Prasad, P. A.; Natarajan, S.; Rao, C. N. R. *Angew. Chem., Int. Ed.* **2000**, *39*, 3470. Rao, C. N. R.; Vaidhyanathan, R.; Natarajan, S. *Chem. Mater.* **2001**, *13*, 3524.
- (87) Adair, B. A.; Diaz Delgado, G.; Delgado, M.; Cheetham, A. K. *Solid State Sci.* **2000**, *2*, 119. Riou, D.; Baltazar, P. M.; Férey, G. *Solid State Sci.* **2000**, *2*, 127.
- (88) Vaidhyanathan, R.; Natarajan, S.; Rao, C. N. R. *Chem. Mater.* **2001**, *13*, 185. Reineke, T.; Eddaoudi, M.; Fehr, M.; Kelley D.; Yaghi, O. M. *J. Am. Chem. Soc.* **1999**, *121*, 1651. Dong, Y. B.; Smith, M. D.; zur Loye, H. C. *Solid State Sci.* **2000**, *2*, 335. Dong, Y. B.; Smith, M. D.; zur Loye, H. C. *Solid State Sci.* **2000**, *2*, 861.
- (89) Yaghi, O. M.; O'Keeffe, M.; Kanatzidis, M. (Editors) *J. Solid State Chem.* **2000**, *152*, 1–321.
- (90) Hagrman, D.; Hagrman, P. J.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 3165.
- (91) Zeng, L. M.; Wang, Y.; Wang, X.; Korp, J. D.; Jacobson, A. J. *Inorg. Chem.* **2001**, *40*, 1323.
- (92) Endo, K.; Sawaki, T.; Koyanagi, M.; Kobayashi, K.; Masuda, H.; Aoyama, Y. *J. Am. Chem. Soc.* **1995**, *117*, 8341.
- (93) Férey, G.; Cheetham, A. K. *Science* **1999**, *283*, 1125.
- (94) Férey, G. *J. Solid State Chem.* **2000**, *152*, 37.
- (95) Loiseau, T.; Retoux, R.; Lacorre, P.; Férey, G. *J. Solid State Chem.* **1994**, *111*, 427.
- (96) Cavellec, M.; Egger, C.; Linares, J.; Nogues, C.; Varret, F.; Férey, G. *J. Solid State Chem.* **1997**, *134*, 349.
- (97) Li, H.; Laine, A.; O'Keeffe, M.; Yaghi, O. M. *Science* **1999**, *283*, 1145 and references therein.
- (98) Cahill, C. L.; Ko, Y.; Parise, J. B. *Chem. Mater.* **1998**, *10*, 19 and references therein.
- (99) Scott, R. W. J.; MacLachlan, M. J.; Ozin, G. A. *Curr. Opin. Solid State Mater. Sci.* **1999**, *4*, 113 and references therein.
- (100) Kim, K. W.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1992**, *114*, 4878. *J. Am. Chem. Soc.* **1998**, *120*, 8124.
- (101) Magneli, A. *Acta Chem. Scand.* **1953**, *7*, 315.
- (102) Paulet, C.; Loiseau, T.; Férey, G. *Chem. Commun.* **2000**.
- (103) Davis, M. E.; Saldarriaga, C.; Montes, C.; Garces, J. M.; Crowder, C. *Nature* **1998**, *391*, 698.
- (104) Livage, C.; Egger, C.; Férey, G. *Chem. Mater.* **1999**, *11*, 1546.
- (105) Dautant, A.; Langlois d'Estaintot, B.; Gallois, B.; Brown, T.; Hunter, W. N. *Nucl. Acids Res.* **1995**, *23*, 1710.
- (106) Cronin, L.; Kögerler, P.; Müller, A. *J. Solid State Chem.* **2000**, *152*, 57.
- (107) Müller, A.; Das, S. K.; Krickemeyer, E.; Kögerler, P.; Bögge, H.; Schmidtman, M. *Solid State Sci.* **2000**, *2*, 847.
- (108) Khan, I. *J. Solid State Chem.* **2000**, *152*, 105.
- (109) Férey, G. *Science* **2001**, *285*, 994.
- (110) O'Keeffe, M.; Eddaoudi, M.; Li, H.; Reineke, T.; Yaghi, O. M. *J. Solid State Chem.* **2000**, *152*, 3.
- (111) Chen, B.; Eddaoudi, M.; Hyde, S. T.; O'Keeffe, M.; Yaghi, O. M. *Science* **2001**, *285*, 1021.
- (112) Akporiaye, D.; Dahl, I. M.; Karlsson, A.; Wendelbo, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 609.
- (113) Lewis, D. W.; Willock, D. J.; Catlow, C. R. A.; Thomas, J. M.; Hutchings, G. J. *Nature* **1996**, *382*, 604.
- (114) Schbn, J. C.; Jansen, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1286.
- (115) Mellot Draznieks, C. F.; Newsam, J. M.; Gorman, A. M.; Freeman, C. M.; Férey, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 2270.