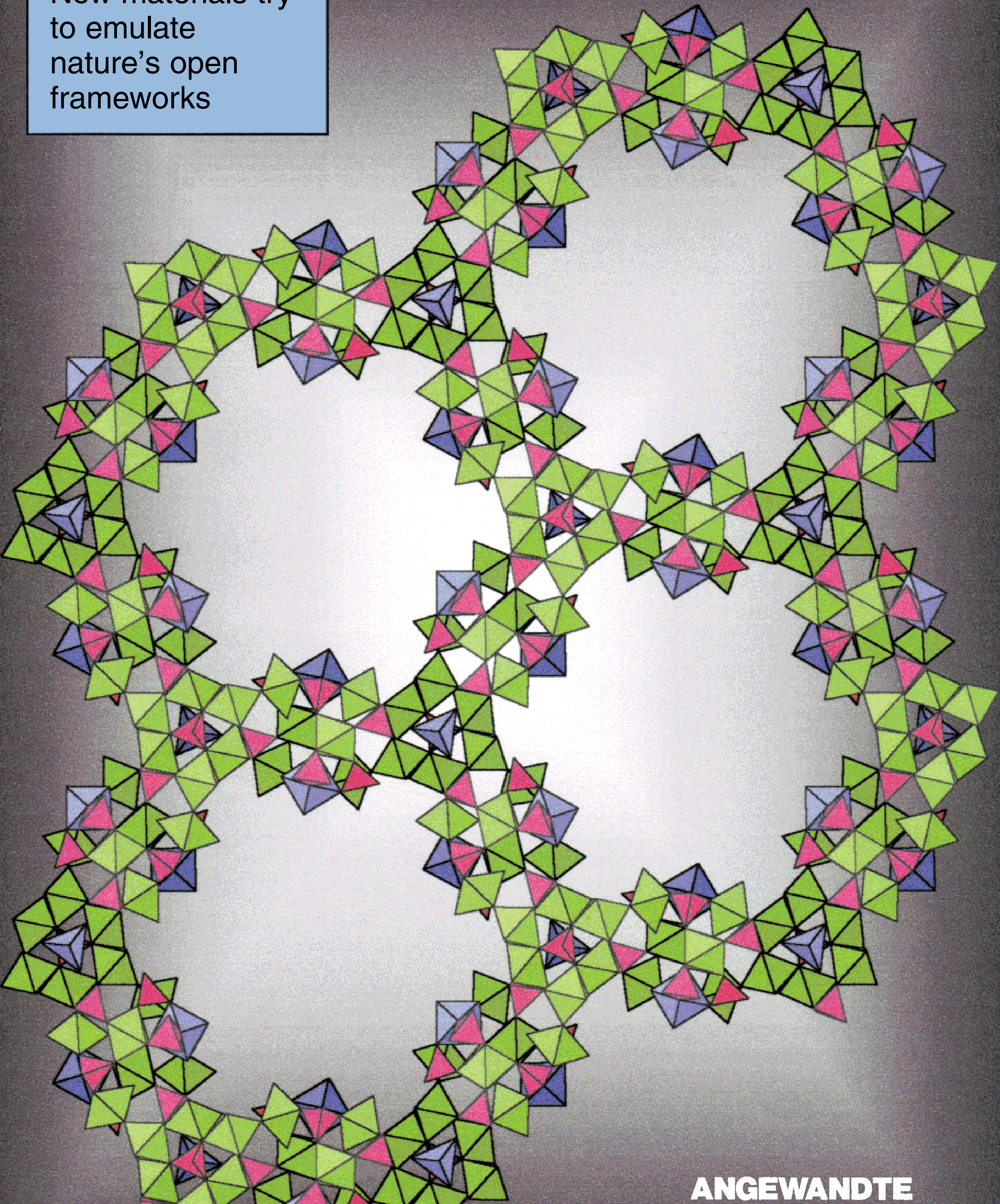
New materials try to emulate nature's open frameworks



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Open-Framework Inorganic Materials

Anthony K. Cheetham,* Gérard Férey,* and Thierry Loiseau

In memory of Jean Rouxel

The field of open-framework inorganic materials has expanded dramatically during the last decade. The scope of such materials is no longer limited to aluminosilicate zeolites, aluminum phosphates and related systems, but now embraces frameworks based upon as many as 25 elements of the periodic table. These include a large number of main block phosphates, such as those of gallium, indium, and tin, as well as several transition metal phosphates, including systems based upon vanadium, molybdenum, cobalt, and iron. In addition to oxide-containing phases, open frameworks are now being found in the realm of sulfides, chlorides, and nitrides, as well as in coordination compounds. Applications of open-framework materials continue to be dominated by the aluminosilicate zeolites, which are noted for their stability and which find utility in catalysis, separations, and ion-exchange, but attempts are being made to exploit some of the exciting properties of the newly discovered systems. The review discusses the synthesis and structures of this growing class of materials, as well as some of their properties and applications.

Keywords: host–guest chemistry · microporosity · solid-state structures · zeolite analogues · zeolites

1. Introduction

There has been an enormous growth in the chemical diversity of open-framework inorganic materials during the 1990s. Prior to the early 1980s, when the nanoporous aluminum phosphates were first reported by Flanigen and co-workers, the aluminosilicate zeolites and closely related systems represented the predominant class of open-framework materials with three-dimensional crystalline structures. The extent of the change during the last 16 years can be judged from the fact that as many as 25 chemical elements of the main block and the transition series are now known to participate as major components of such frameworks, and the number is increasing rapidly. Most are based upon oxygen-containing materials, especially phosphates, but there is a growing list of examples based upon other chemistries, such as oxyfluorides, nitrides, and sulfides. The range of systems has also increased in another sense: whereas the zeolites and early aluminophosphates were based entirely upon corner-sharing tetrahedra ($[SiO_4]$, $[AlO_4]$ etc.), many of the newer architectures involve other polyhedra such as octahedral $[XO_6]$, pentacoordinated $[XO_5]$, or pyramidal $[XO_4]$ or $[XO_3]$ units. These exciting developments will gradually have an impact on the applications of such materials. The traditional applications of aluminosilicate zeolites are in the areas of ion-exchange, separations, and catalysis, but the new generation of materials offers a wider range of chemical and physical properties that are only just beginning to be explored.

The scope of the present review is restricted for practical purposes to three-dimensional open-framework inorganic structures, thus excluding a large range of related materials such as clays, layered phosphates, and organic frameworks such as clathrates and cyclodextrins. Nor shall we discuss pillared layer structures since these are probably better treated in the context of clays. Our coverage is also limited to crystalline open frameworks, rather than nonperiodic porous systems such as xerogels and aerogels. It does, however, embrace both true nanoporous materials—those that show some reversible adsorption and desorption behavior—and open inorganic frameworks from which it has not yet proven possible to remove the contents of the channels without loss of crystallinity and collapse of the framework; this is a common problem that will no doubt be overcome by

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more subtle chemical treatments. The review also includes reference to the "mesoporous", surfactant-mediated structures, albeit in less detail.

The discussion will follow an approximately chronological sequence, beginning, of course, with the zeolites and finishing with a short discussion of the growing number of open-framework coordination compounds. Between these extremes, we shall explore a wide range of chemical systems, including phosphates, oxides, nitrides, chalcogenides, and halides. To a considerable extent, the sequence is also one of decreasing thermal stability. For example, the extensive occurrence of aluminosilicate zeolites and their widespread utility in industry depends heavily upon the thermodynamic and kinetic stability of the constituent aluminosilicate framework (it should be noted that the open frameworks of zeolites are thermodynamically slightly less stable than the corresponding condensed structures, into which they will transform during severe thermal treatment). The challenge with many of the newer materials is that their stability with respect to transformation into alternative condensed structures is considerably lower. Nevertheless, there are many surprises in this respect, such as the unusual stability of the Sn^{II} phosphates and rare-earth dicarboxylates.

Given the huge literature in this burgeoning area, we shall not attempt to give a comprehensive coverage, but we shall endeavor to highlight the important general trends and to give an eclectic selection of illustrative examples and references. More recent developments will be given greater emphasis since they have not been reviewed in detail elsewhere.

2. Aluminosilicate Zeolites and Related Materials

The aluminosilicate zeolites of general formula $A_{x/n}$-$[Si_{1-x}Al_xO_2] \cdot m\,H_2O$, where A is typically a metal cation of valence n, were the first class of nanoporous materials to be recognized. They occur quite extensively in nature, and synthetic examples were made as early as the mid 19th century.[1] Such has been the rate of development in this area during the second half of the 20th century that as many as 100 different architectures are now known,[2] all of which are based upon vertex-sharing $[SiO_4]$ and $[AlO_4]$ tetrahedra, as in the example shown in Figure 1.[*] The Si/Al ratio can range from a minimum of 1 (where the Si and Al would be in strict alternation) to infinity (see below). The nomenclature is often confusing, in spite of the fact that the International Zeolite Association has assigned a three-letter code to each structure type. A typical example would be FAU, which represents the family of materials with the faujasite-type structure. Never-

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[*] All black–and–white figures are shown on approximately the same scale in order to facilitate comparisons between their pore dimensions.

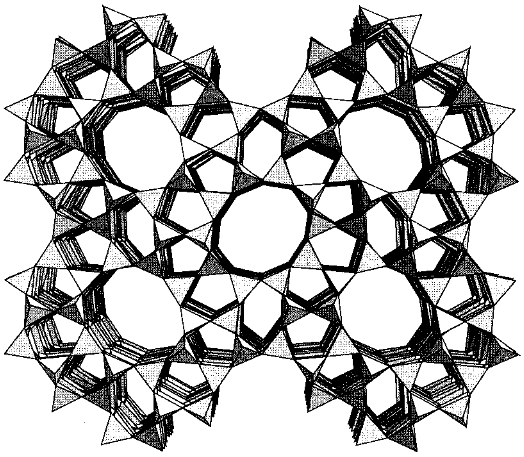

Figure 1. A perspective view of the structure of zeolite ZSM-5 (MFI), viewed down the straight channel; no cations are shown. The tetrahedra are shaded for clarity.

theless, many materials are more commonly known by acronyms chosen by the laboratories in which they were discovered. Pore sizes range from about 2.5 Å in the case of sodalites (SOD), in which the largest channel has rings containing 6 Si/Al sites (i.e. 6-rings), to about 10 Å in so-called UTD-1 which has a 14-ring channel[3] (Figure 2). Some common examples are given in Table 1. Zeolitic materials, of course, are well known to exhibit large pore volumes that are associated with very low tetrahedral (T) site densities (<20 T atoms/1000 Å^3, T = Si,Al). The majority of the systems with large channels contain rings with even numbers of T sites, for example 8-, 10-, 12- or 14-rings, but a recent X-ray diffraction study found both 7- and 9-rings in the high-silica zeolite SSZ-23.[4]

Table 1. Examples of nanoporous aluminosilicates, with the three-letter IZA designations and a brief description of the pore systems.

System	Pore system
sodalite family (SOD) (e.g. mineral and synthetic sodalites)	3-dimensional; 6-ring channels
zeolite A family (LTA) (e.g. zeolites A, ZK-4; no mineral analogue)	3-dimensional; 8-ring channels
chabazites (CHA) (e.g. mineral chabazites, SSZ-13)	3-dimensional; 8-ring channels
ZSM-5 (MFI) (e. g. mineral murataite, silicalite)	2-dimensional; 10-ring channels
ferrierites (FER) (e.g. mineral and synthetic ferrierites)	2-dimensional; 10 and 8-ring channels
faujasites (FAU) (e.g. mineral faujasite, zeolites LSX, X, Y, US-Y)	3-dimensional; 12-ring channels

Industrial interest in these materials has been driven by their excellent ion-exchange properties in the hydrated state, and by the exciting adsorption and catalytic properties exhibited by their dehydrated forms. Indeed, it is for this reason that many of the most eye-catching synthetic discoveries have been made in industrial laboratories, such as those of Mobil, Union Carbide (now UOP), British Petroleum, and Chevron. Table 2 summarizes some of the most important actual and prospective applications. Commercial production of zeolites was approximately one million tons in 1995, most of which was accounted for by applications in catalytic cracking, xylene isomerization, and detergents. This pattern is gradually changing, however, as new applications are developed.

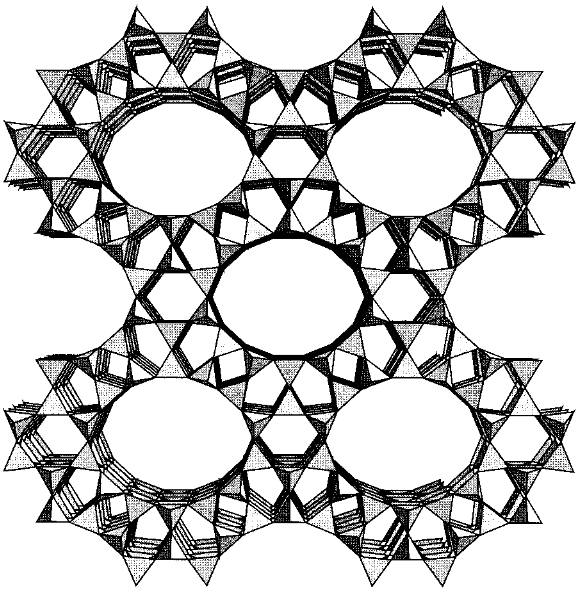

Figure 2. A perspective view of the structure of zeolite UTD-1; no cations are shown.

Table 2. Some important applications of aluminosilicate zeolites.

Well-established:
ion-exchange with hydrated zeolites
detergency (e.g. zeolites Na-A and Na-P)
water softeners
animal feeds
radwaste remediation (e.g. Cs, Sr with clinoptilolite)
molecular sieving with dehydrated zeolites
air separation (N_2 from O_2 with Li-LSX)
drying agents (e.g. double glazing, air conditioning)
sulfur removal from natural gas
separation of HFCs (CFC substitutes)
catalysis with dehydrated zeolites
catalytic cracking (gasoline production)—zeolite-Y derivatives
xylene isomerization (for polyesters)—H-ZSM-5
butene isomerization—H-FER
methanol to gasoline—H-ZSM-5
phenol to hydroquinone—titanosilicates
denox reactions—Cu-ZSM-5, Co-FER
Future possibilities include:
nano-composites for electro-opticals
sensors with zeolite thin films
stereoselective polymerization
contrast enhancement in MRI (e.g. Gd-Y)

Hydrated low-silica zeolites (Si/Al <2), such as synthetic sodium zeolite A (LTA), are used widely for ion-exchange applications where their high cation content leads to high exchange capacities. Many other factors, such as cost, good kinetics, and selectivity, are also important. Consequently, cheap naturally occurring materials with somewhat higher Si/Al ratios (3–5), for example clinoptilolite (HEU) and phillipsite (PHI), may be used for certain large-scale applications. Dehydrated forms of the large-pore low-silica zeolites, such as zeolite X (FAU), are used in adsorption and separation applications, including noncryogenic air separation (Li-zeolite LSX). The interactions between the under-coordinated cations and the sorbate molecules are a crucial feature of such processes. In air separation, for example, it is the affinity of the lithium for the dinitrogen molecule, which has a quadrupolar moment three times bigger than that of dioxygen, that provides the basis for the separation.[5] The low-silica materials are relatively unstable at high temperatures, so materials with high Si/Al ratios are preferred for catalytic applications. These include high-silica faujasite types such as ultrastabilized Y, and ZSM-5. Most of the catalytic processes are based upon acid-catalyzed reactions in which the exchangeable cation of the zeolite is replaced by a proton that provides Brønsted acidity. In addition, the shape and size of the zeolite cavities leads to selectivity in the reaction, hence the term "shape-selective catalysis". This is the case in the hydrocarbon cracking catalysts used in gasoline manufacture and the isomerization catalysts used in *p*-xylene production for polyester manufacture. Some of the new titanosilicates, such as TS-1 (MFI) which contains framework titanium, exhibit redox activity and are being used for partial oxidation reactions involving phenols and hydrogen peroxide.[6]

Naturally occurring zeolites normally have quite low Si/Al ratios, typically three or less, and it is often quite easy to make synthetic analogues of these materials under hydrothermal conditions. For example, synthetic analogues of the mineral faujasite (FAU) can be made from reactions between sodium silicate and sodium aluminate under basic conditions at 60–150 °C. Variations in the temperature, charge-compensating cation, time of reaction, and the pH value, amongst other variables, yield a variety of low-silica aluminosilicate zeolites, although all such reactions are carried out under basic conditions. Post-synthesis modifications, such as steaming or treatment with silicon tetrachloride, have been developed to increase the Si/Al ratios of these materials to render them stable during high-temperature use. A major breakthrough in respect of the direct synthesis of high-silica materials took place in the late 1960s with the development of synthetic routes involving the hydroxides of quaternary ammonium ions or organic amines in place of the normal alkali metal bases. These organic nitrogen compounds, which act as template molecules or structure-directing agents, are incorporated into the final product where they replace the usual charge-compensating cations. They play two important roles: 1) the size and shape of the quaternary amine can lead to the creation of new pore structures which cannot be made in other ways; 2) the large sizes of these cations, when compared with traditional metal cations, means that they can only compensate for a relatively low framework charge, thus leading to the formation of high-silica materials. The organic cations can normally be removed from the zeolite by calcination, leaving behind the acid form of the zeolite (see above). A classical example is zeolite ZSM-5 (Figure 1), which is made in the presence of tetrapropylammonium cations, TPA (it should be noted that organic templates are not always essential for the synthesis of high-silica zeolites; for example, ZSM-5 itself can be prepared by a template-free method). Curiously, over 20 years after its full characterization in the laboratory,[7] a natural analogue of ZSM-5, known as murataite, has recently been discovered.[8] It has a Si/Al ratio of 7.6, which is the highest found in any natural zeolite.

In addition to the aluminosilicates zeolites, some synthetic analogues, such as borosilicates, gallosilicates, and ferrisilicates have also been explored. The borosilicates are more difficult to prepare, probably because the much smaller boron atom, with its tendency towards planar threefold coordination, is not such an obvious substitute for the aluminum. Gallium- and iron(III)-containing materials, however, are well known and usually have properties similar to those of the aluminosilicates. There is evidence, nevertheless, for some unique behavior with gallosilicates, as in their ability to catalyze cyclization reactions and to activate methane.[9] Other silicate-based systems include the eye-catching titanosilicates, mentioned earlier, and an unusual zincosilicate (VPI-7) which contains tetrahedral Zn^{2+}.[10]

Another interesting development has been the direct synthesis of pure silica materials with no exchangeable cations. The synthesis of the silica polymorphs, which include silicalite-1 (MFI)[11] and siliceous ferrierite (FER),[12] requires template molecules or structure-directing agents, and there is an interesting question as to how the charge of the quaternary ammonium ions is compensated in the absence of framework aluminum. The use of fluoride ion during these reactions is often desirable, and it is known that it can play a variety of roles, for example as a mineralizing agent. Its use is even more widespread in the case of phosphates, as described in Section 3. Since the silica polymorphs should be completely ordered once the organic molecule has been removed, they provide excellent vehicles for detailed characterization by ^{17}O and ^{29}Si NMR spectroscopic studies,[13] as well as for computer simulation studies.[14] They are also very interesting candidates in the context of low-dielectric materials for integrated circuit manufacturing,[15] since they can be made defect-free and have up to nearly 50 % pore volume.

There remains considerable interest in the synthesis of new zeolite architectures that may offer unique catalytic or other applications, and much of the synthetic effort lies in the area of the use of novel quaternary ammoniums ions as structure-directing agents. In this respect, the most eye-catching discovery in the last ten years has been the successful use of self-assembling surfactant cations, such as $(C_{16}H_{33})(CH_3)_3N^+$, in such reactions by scientists at Mobil.[16] This can lead to the formation of lamellar, hexagonal, or cubic phases, known collectively as the M41S family, and which are closely related to the lyotropic phases formed by simple halide salts of these cations in aqueous solution. Calcination of the hexagonal and cubic phases has yielded thermally stable porous materials with pores that are much larger (approx. 30–100 Å) than those of conventional zeolites. Although these materials are periodic in terms of their pore structures and therefore give rise to coherent X-ray diffraction, the silica walls are disordered and more resemble the structure of a glass. There has been a lot of discussion concerning the mechanism of the formation of the M41S materials[17] and their possible applications. Unlike conventional zeolites they do not exhibit strong acidity, but they do show promise as supports in other types of catalytic reactions, such as olefin polymerizations.[18] Recent reviews of the area[19, 20] also discuss the extension of this type of chemistry to other chemical systems, where a large number of analogues have now been reported (e.g. mesoporous $AlPO_4$, TiO_2, Al_2O_3, metallic platinum, and so on).

It has been shown both experimentally[21] and theoretically[14] that open structures are less stable than their condensed analogues, but the differences are quite small, about $15\,kJ\,mol^{-1}$ between siliceous faujasite and α-quartz for example. The remarkable thermal stability of silica-based nanoporous materials, therefore, stems from the strength of their T–O bonds (e.g. Si–O $\approx 466\,kJ\,mol^{-1}$) which render them stable with respect to framework rearrangement. As we look at other chemical systems in the following sections, we shall see that this kinetic stability is less evident as the framework bonds become weaker. Consequently, whereas it is now practicable in many systems to make open-framework materials with organic cations in the channels, it is often very difficult to remove these guests without inducing the collapse of the host structure. The vast majority of the systems that we shall describe cannot therefore be rendered nanoporous. One family that approaches the stability of the silicates, however, is the aluminum phosphates ($AlPO_4$), which are discussed in the following section.

3. Aluminum Phosphates, Gallium Phosphates, and Related Materials

3.1. Aluminum Phosphates

Following the extensive development of synthetic, microporous aluminosilicates, research has gradually shifted towards the exploration of new families of three-dimensional frameworks. Based on crystal chemistry principles, the aluminophosphates ($AlPO_4$) were considered first. They are isoelectronic with SiO_2 and can be regarded as III–V analogues. Seven allotropic forms of $AlPO_4$ that correspond to condensed silica polymorphs are known (α- and β-quartz, α-, β-, and γ-tridymite, and α- and β- cristobalite).[22] In these materials, aluminum and phosphorus are observed in tetrahedral coordination, as is silicon in the silicas. From these considerations, Flanigen and co-workers at Union Carbide Corporation discovered a new generation of microporous materials, aluminophosphate $AlPO_4$-*n* (*n* refers to a structural type), at the beginning of the 1980s.[23] These materials, and related ones made subsequently, are the subject of this section.

The synthetic procedure[24] is similar to that used for zeolites: the aluminophosphates are prepared hydrothermally under autogenous pressure in the temperature range 100–250 °C. They are typically obtained from a mixture of aluminum oxyhydroxide or alkoxide and phosphoric acid in water, leading to the formation of an aluminophosphate gel. An amine or quaternary ammonium salt, which plays a templating or structure-directing role, is then added to the mixture. These reactions are typically carried out in the following molar proportions: $x\,R{:}1\,Al_2O_3{:}1.0 \pm 0.2\,P_2O_5{:}y\,H_2O$ ($0 < x < 10$, $40 < y < 400$), where R is the structure-directing species. The crystallization time depends on multiple variables such as temperature, reactant composition, and structural type, and ranges from several hours to several weeks. The pH of the reaction, which is less than that observed in zeolite synthesis, varies within the range from 3 to 10 and tends towards the neutral value at the end of the reaction. The organic molecule, which is trapped within the pores, plays a critical role in producing the microporous framework. In the absence of such a molecule, only dense $AlPO_4$ or $AlPO_4 \cdot n\,H_2O$ hydrates are formed. The thermal stability of the open-framework solids is similar to that obtained for zeolites and the template can often be removed by calcination in air at 500–600 °C. Some compounds exhibit stable structures up to 1000 °C. In the $AlPO_4$-*n* series, the Al/P ratio is 1 and the frameworks are electrostatically neutral.

Investigations were then performed on the incorporation into the $AlPO_4$ frameworks of elements with different valences in order to modify the chemical properties for catalysis, ion-exchange, and so on. This led the Union Carbide researchers to synthesize several new series of materials, in particular the silicoaluminophosphates (SAPO-*n*),[25] metalaluminophosphates (MAPO-*n*) and metalsilicoaluminophosphates (MAPSO-*n*).[26] The strategy was first to explore divalent cations which are able to adopt tetrahedral coordination (e.g. $M = Mg^{2+}$, Mn^{2+}, Fe^{2+}, Co^{2+}, and Zn^{2+}). The weakly acidic pH of the reaction prevents the precipitation of the metal as hydroxide or oxide and facilitates its partial incorporation into the inorganic framework. These phases have framework compositions of the general formula $(Si_xM_wAl_yP_z)O_2$, where x varies from 0 to 0.20 and w from 0 to 0.25. The silicon substitutes preferentially at the phosphorus site whereas the metal substitutes exclusively for the aluminum. The introduction of these elements renders the frameworks negative and therefore charge-compensating cations are required, as in the aluminosilicate zeolites. When these cations are protons, the materials exhibit acid catalytic properties which vary as a function of the structural type and the nature of the substituting element.[27] The incorporation of other elements, such as monovalent (Li), divalent (Be), trivalent (B, Cr, Fe, Ga), tetravalent (Ti, Ge), and pentavalent elements (As), into the $AlPO_4$ framework has also been reported (e.g. AlAsPO-*n*).[28]

From the structural point of view, the microporous aluminophosphate-based compounds include more than 40 different framework types. As in the zeolites, the three-dimensional structure is delimited by channels and cavities where the templating agent is located. However, there are some differences compared with the topologies encountered in the zeolite family. The majority of the aluminum phosphate based solids exhibit (4,2)-connected networks with alternating Al and P on tetrahedral sites. This rule limits the structural possibilities because rings must be formed by an even number of T atoms, which prevents the occurrence, for example, of 5-ring units. Thus, while the aluminophosphate analogues of the aluminosilicate zeolites, erionite (ERI) or sodalite (SOD), are known ($AlPO_4$-17 and $AlPO_4$-20, respectively[2]), no $AlPO_4$ exists with the MFI type structure, which contains

5-ring units. In the last issue of the *Atlas of Zeolite Structure Types*,[2] 16 structural types were reported for both the silicate and phosphate families.

During the last decade, the synthesis of microporous aluminophosphate-based materials has led to the discovery of numerous novel topologies, some of them exhibiting extra-large pores delimited by more than 12 T atoms (until recently, the pore sizes found in aluminosilicates ranged only up to 12-rings, but the synthesis of the silicate UTD-1 pushed the limit to 14; see Section 2). For the $AlPO_4$s, this trend was initiated at the end of the 1980s by Davis and co-workers with the synthesis of the aluminophosphate VPI-5 (VFI).[29] This molecular sieve contains one-dimensional circular channels with an 18-membered ring aperture and possesses a free diameter of 12–13 Å (Figure 3). The VFI network can be viewed as the insertion of two adjacent 4-ring units between the 6-ring units of $AlPO_4$-tridymite. The structure of $AlPO_4$-8 (AET),[30] which contains 14-ring channels, is a close relative of the VPI-5 network.

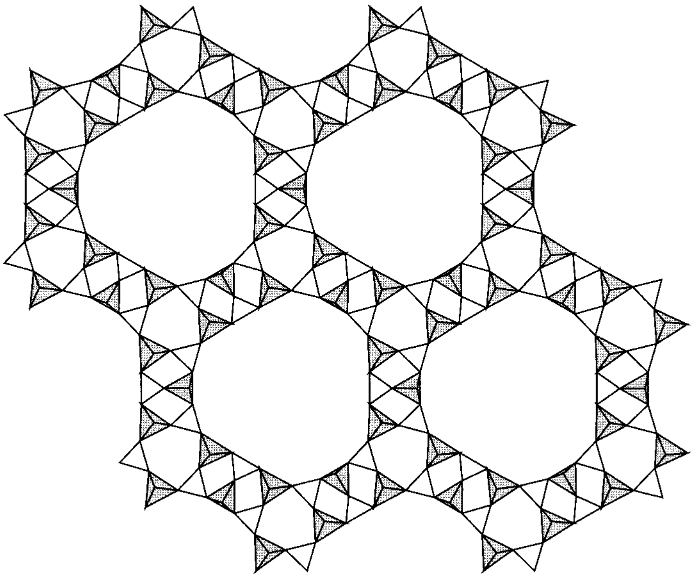

Figure 3. A plan view of the structure of the aluminophosphate VPI-5 (VFI).

The occurrence of coordination numbers greater than four for the aluminum is another feature of the phosphate-based solids in comparison with the zeolites. For example, in some phases aluminum adopts fivefold (trigonal bipyramidal) or sixfold coordination (octahedral). In these cases, water groups or anionic species such as hydroxide complete the coordination sphere of the aluminum, which leads to connection modes already encountered in mineral aluminum phosphates[31] in which $[AlO_n]$ polyhedra may share corners or edges through Al-O-Al linkages. It also results in the formation of odd-numbered rings, as in, for instance, $AlPO_4$-14A[32] and $AlPO_4$-21 (Figure 4).[33] In these examples, the channel size appears to be limited as a consequence of the increase of the aluminum coordination, which thus seems to be a drawback for the production of large pores.

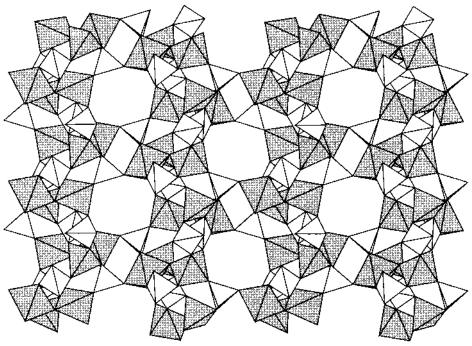

Figure 4. A plan view of the structure of $AlPO_4$-21.

3.2. Gallium Phosphates—Early Developments

In the mid-1980s, research was extended to microporous phosphates in which other elements completely replaced aluminum. For example, Parise[34–36] described the synthesis of several gallophosphates related to the $AlPO_4$-*n* family. Following this idea, Xu and co-workers[37–40] undertook a systematic study in the gallium system to produce a series named $GaPO_4$-Cn (n = 1–12). Some of them are identical to the $AlPO_4$-*n* materials; for example, $GaPO_4$-C7[39] is isostructural with the hydrated gallium phosphate $GaPO_4 \cdot 2H_2O$[41] and the $AlPO_4$-15[42] type, and corresponds to the structure of the iron phosphate mineral, leucophosphite.[43] However, a new framework called $GaPO_4$-C3,[37] previously reported as $GaPO_4$-α by Wilson et al.,[44] has been shown to exhibit an open structure containing 8-ring channels. In this program,[40] some alumino- and galloarsenates with new topologies were also described ($AlAsO_4$-1,[45] $AlAsO_4$-2[46] and $GaAsO_4$-2[47]). These examples indicate that gallium can be found in four-, five- and sixfold coordination in its phosphates, as is the case for aluminum in the aluminum compounds. However, there is a general trend for the coordination numbers to be higher than those of aluminum.

The micropores of these early phosphate and arsenate frameworks are limited to 8-ring channels, except for the gallium arsenate $GaAsO_4$-2[47] which has tunnels delimited by ten polyhedra (but see Section 3.4). A deviation from the normal Ga/P stoichiometry of 1 is shown in the hydrated gallophosphate $Na_3Ga_5(PO_4)_4O_2(OH)_2 \cdot 2H_2O$.[48] The pores of the structure contain sodium cations and water molecules, and the latter can be desorbed to give rise to pores with an aperture diameter of 4 Å.

3.3. Reactions in Nonaqueous Solvents

All of the phosphate compounds described so far were synthesized with water as the main solvent. Several studies (principally by the groups of Xu of Jilin, China, and Thomas of the Royal Institution, London) have explored the solvent effect under hydrothermal conditions for the feasibility of making open frameworks and for the control of the crystal quality.[49] The tested solvents were mainly alcohols (butanol, triethylene glycol, etc.) and improved crystallization is generally observed, which is helpful for X-ray structural characterization. Several known aluminophosphates, including $AlPO_4$-5, $AlPO_4$-11, and $AlPO_4$-21, have also been synthesized from nonaqueous systems.[50] In many cases, however, low-dimensional AlPOs and GaPOs[51] were obtained, corresponding to several series of layered and chain solids, with P/Al or P/Ga ratios ranging from 4/3 to 2/1, in which the interlamellar or interchain space is occupied by organic cations. In a recent examination of the formation of aluminophosphates under nonaqueous conditions, Ozin and co-workers[52] have suggested that intermediates based upon one-dimensional chains could be involved in the crystallization of two-dimensional porous layers and finally the three-dimensional open-framework materials. The condensation scheme is believed to depend upon the hydrolysis rate determined by the water concentration present in the reaction mixture.

The utilization of organic solvents has nevertheless allowed for the discovery of several new three-dimensional structural types. An aluminophosphate known as JDF-20,[53] $[Al_5P_6O_{24}H]^{2-} 2[N(C_2H_5)_3H]^+ \cdot 2H_2O$, has been obtained from a mixture of triethylene glycol and triethylamine. Its framework is three-dimensional and contains 20-rings with elliptical apertures with a free diameter of 6.2 by 14.5 Å (Figure 5). The other feature is the P/Al ratio, which differs from 1, as is sometimes the case in other microporous aluminophosphates. All of the $[AlO_4]$ tetrahedra share their vertices, but this is not the case for the phosphate groups, some of which exhibit terminal P–OH bonds to give rise to an interrupted framework. The utilization of ethanolamine instead of pure amine was reported for the synthesis of the microporous aluminophosphate $AlPO_4$-JDF,[54] analogous to $AlAsO_4$-1,[45] in the presence of a large variety of alcohols. The use of alcoholic solvents has continued to yield interesting $AlPO_4$ materials, as shown by the recent preparation of AlPO-HDA.[55]

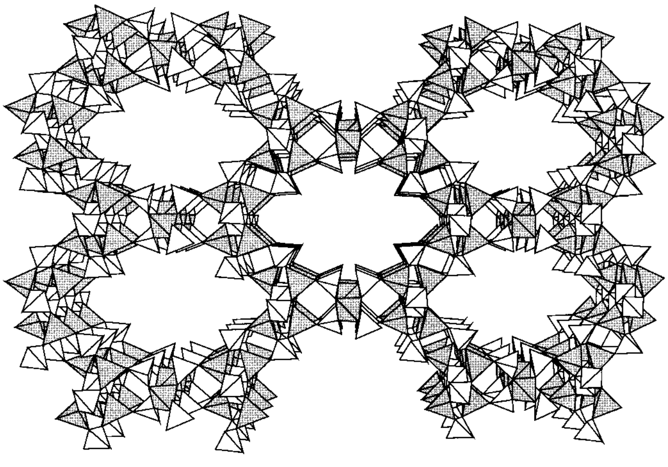

Figure 5. A perspective view of the structure of JDF-20.

The first gallium phosphates prepared from predominantly nonaqueous solvents were the two $GaPO_4$ materials, $GaPO_4$-M1 and $GaPO_4$-M2, obtained by variation of the methylamine content in ethylene glycol.[56] The structure of $GaPO_4$-M2[57] is unique and consists of 8-ring channels with the methylammonium cations in the cavities. Another compound, $[Me_2NH(CH_2)_2NHMe_2]^{2+}[Ga_4P_5O_{20}H]^{2-} \cdot H_2O$,[58] presents an open framework with large elliptical pores characterized by puckered windows (16.50 × 6.65 Å) made of 16 Ga/P atoms.

3.4. The Fluoride Method

The fluoride method, previously mentioned in Section 2, was first used in the elaboration of phosphate-based compounds by Kessler and co-workers.[59, 60] Beside its mineralizing effect, fluoride seems to have a catalytic role: for example, the presence of fluoride ions is necessary for the formation of the phase $AlPO_4$-14A,[61] although it is not incorporated into the network. However, when fluoride is present in the structure, it can adopt specific configurations in which $AlPO_4$ structural types are essentially preserved. For example, in $AlPO_4$-5 (AFI)[62] the fluoride is located between two 4-rings in the 4-ring columns. It is linked to two aluminum atoms with rather long distances (Al–F 2.19 Å). In the aluminophosphate analogues of the zeolites chabazite (CHA)[60, 63] and gismondine (GIS),[64] two fluoride atoms bridge two aluminum atoms across the 4-ring units, rendering them octahedrally coordinated rather than tetrahedrally coordinated as in the aluminosilicate forms. Double octahedral entities, $[Al_2O_8F_2]$, are thus generated with a common F–F edge (Figure 6a).

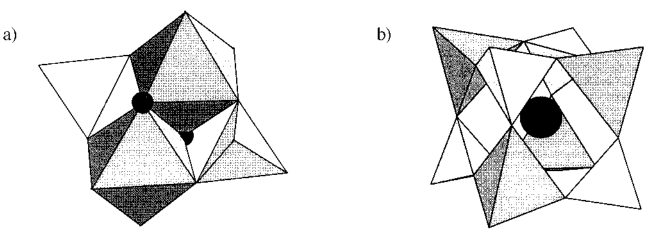

Figure 6. a) A representation of the unit $[M_2(PO_4)_2F_2]$ (fluorides are shown as filled circles). b) A representation of a D4R cage with an encapsulated fluoride anion (fluoride is shown as a filled circle).

The most exciting feature of the fluoride method is its use in the synthesis of new alumino- and gallophosphate architectures which incorporate fluorine atoms into the open framework. Two situations are found for the fluoride. First, it seems to stabilize the double-4-ring (D4R) cage, which is a cube with the corners occupied by $[TO_4]$ tetrahedra. The fluoride is trapped within this cavity (Figure 6b) and Kessler has suggested that such fluoride ions could play a structure-directing role. This case is encountered in GaPO-LTA,[65] but the major breakthrough was the discovery of cloverite (Figure 7),[66] a gallophosphate with extra-large pore openings comprising 20 $[TO_4]$ units and a three-dimensional channel system similar to that in faujasite-type zeolites.[2] The expected pore size is 13.2 Å, but the effective diameter is limited by the presence of terminal hydroxy groups that point towards the centers of the windows. The basic building unit is the D4R cage with an occluded fluoride atom. It is noted that the presence of fluoride strongly modifies the surroundings of the gallium atoms, leading to an increase of the coordination to fivefold (elongated trigonal bipyramid).

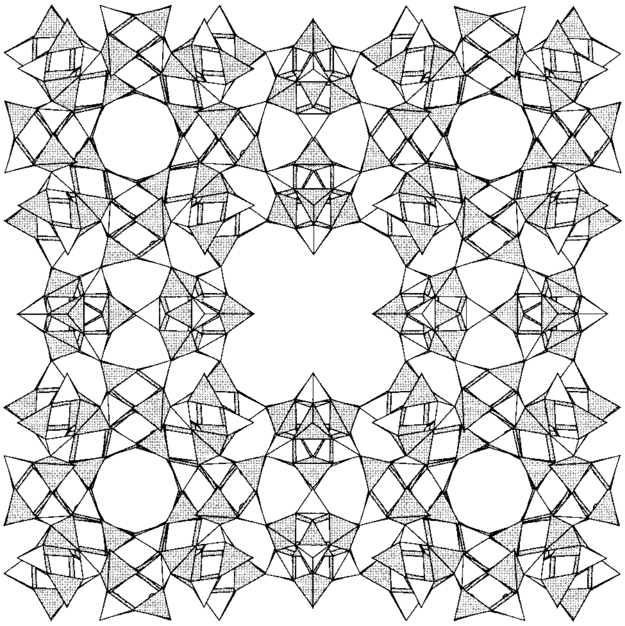

Figure 7. A plan view of the structure of cloverite (CLO).

The resulting Ga–F distances indicate that the fluoride is weakly linked to the gallium atom (Ga–F 2.3–2.6 Å). The occurrence of this octameric unit is also found in aluminophosphates such as $AlPO_4$-16 (AST)[67] synthesized in the presence of hydrofluoric acid. This building unit has also been prepared as an isolated cluster in Mu-1[68] and as linear chains in Mu-3.[69]

Alternatively, fluorine can participate more directly in the coordination sphere of the metal and increase the coordination number from five to six. This is seen in the case of the phosphate CJ2,[70, 71] in which Al or Ga atoms adopt both fivefold and sixfold coordinations. Studies performed by Férey and co-workers[72, 73] in Le Mans gave rise to a new series of oxyfluorinated phosphates called ULM-*n*. In this family, the basic building units can be either tetramers, as is usually found in the crystal chemistry of phosphates,[74] or hexamers (Figure 8a). For the tetramers, the connection of the metal atom is by means of corner- (Figure 8b) or edge-sharing fluorine atoms (Figure 6a). The hexameric unit is quite common in fluorinated materials. It is composed of a central octahedrally coordinated Al or Ga linked to two Al or Ga atom with trigonal-bipyramidal coordination, through fluorine. This trimer is capped by three phosphate groups. The connection of these hexamers generates different packing structures,[75] such as ULM-3 or ULM-4 where the channels are delimited by 10-ring windows. The galloarsenate, $GaAsO_4$-2,[47] exhibits an open framework closely related to that of ULM-4. The hexameric unit can be found with other building blocks, such as the D4R cage in ULM-5 (Figure 9) or the double crankshaft chain in ULM-16 (Figure 10). In the last two compounds, the addition of these other building units leads to the production of extra-large channels with 16-ring windows. The other feature of fluorinated materials is that fluorine in the framework creates anchoring points for the NH groups of the amines as a result of strong hydrogen bonding.

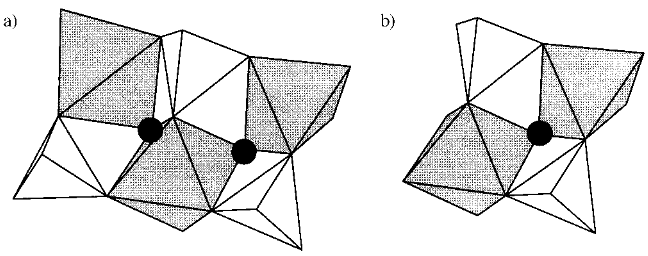

Figure 8. Polyhedral representations of a) the $[M_3P_3]$ hexamer, and b) the $[M_2P_2]$ tetramer.

Synthesis from a predominantly nonaqueous system in the presence of a mixture of HF/pyridine and tris-(2-aminoethyl)-amine (tren) yields another example of a hexameric-based phosphate phase, TREN-GaPO.[76] The structure contains

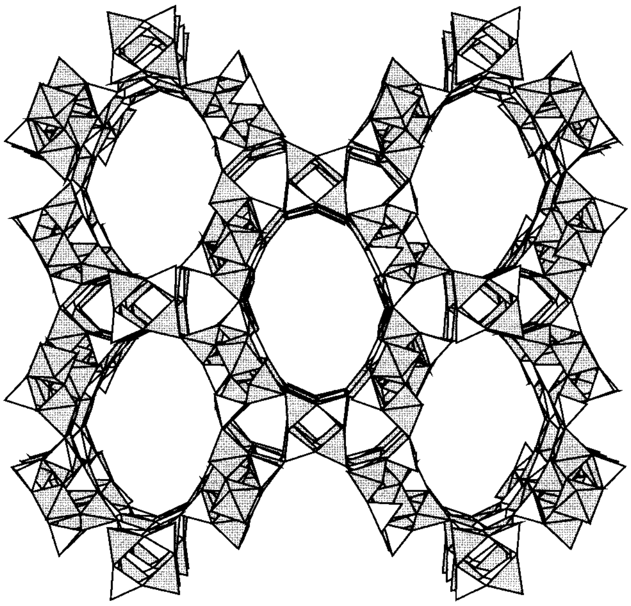

Figure 9. A perspective view of the structure of ULM-5 (without template molecules).

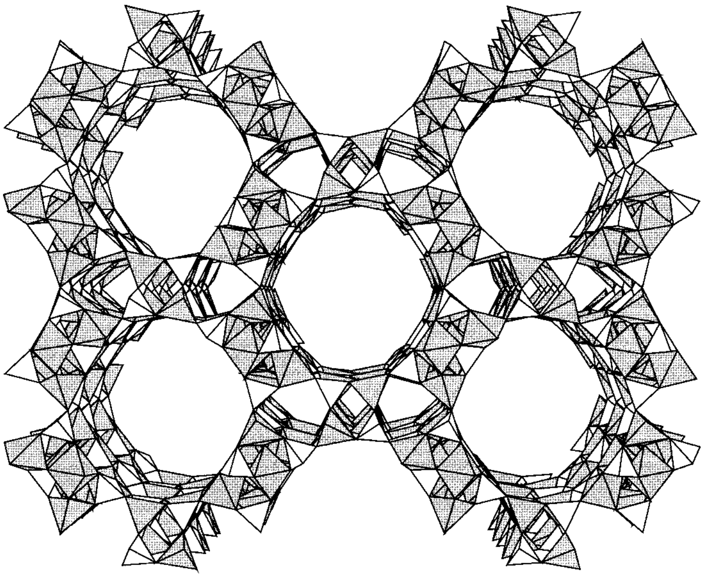

Figure 10. A perspective view of the structure of ULM-16 (without template molecules).

adjacent and parallel 12-ring and 8-ring channels and a segregation is observed between the two amine molecules: the tren molecule is located in the larger channels whereas the pyridine molecule resides in the 8-ring pores (Figure 11). The combined nonaqueous/fluoride reaction strategy, which was first used by Ozin in the synthesis of siliceous zeolite ferrierite,[12] is very versatile. In the gallium system, for example, the use of 1,6-diaminohexane instead of tren led to the formation of a 14-ring channel compound.[77] It should be noted that the pure hexameric-based phosphates were also obtained with aluminum[78] or iron (see Section 5.3) in place of gallium.

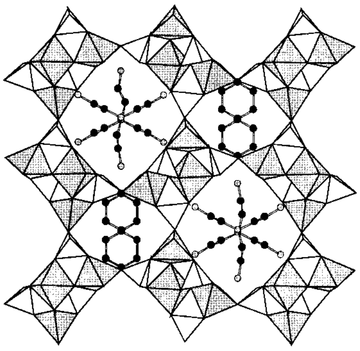

Figure 11. A plan view of the structure of TREN-GaPO (note the pyridine and tren molecules in the small and large channels, respectively). Octahedral $[GaO_6]$ and pentacoordinated $[GaO_5]$ units are shown as shaded polyhedra.

The effect of the fluorine source has also been investigated. Whereas the use of ammonium fluoride leads to the formation of small-pore compounds (e.g. $AlPO_4$-CJ2,[70] $NH_4[Ga_2(PO_4)_2(OH)(H_2O)]\cdot H_2O$[79]), reactions made with a combination of hydrofluoric acid and alkali fluorides (NaF, KF) with alkylammonium hydroxides as organic templates result in the preparation of new phases with larger pores (the UiO-*n* series).[80] For example, UiO-6 (OSI),[81] synthesized with tetraethylammonium hydroxide and NaF or KF, contains one-dimensional 12-ring channels (free aperture 6.2 Å). The alkali cations and fluorine atoms are located in the small pores as in the zeolites, and the fluorine – alkali cation interactions seem to be essential for the formation of this new phase. Without an alkali cation, the use of tetramethylammonium hydroxide leads to a new framework, UiO-7 (ZON),[82] with a two-dimensional 8-ring channel system.

3.5. Synthesis in the Presence of Transition Metal Coordination Complexes

Recently, transition metal coordination complexes have been tested as structure-directing agents in the synthesis of alumino- and gallophosphates. This type of complex is very versatile, and offers a range of unique conformations that are not found with organic amine molecules. Many exhibit chiral character, which might lead to the formation of chiral frameworks for use in enantioselective heterogeneous catalysis or separation processes. Different tris(diamine) cobalt(III) complexes have been tested and a few chiral layered aluminophosphates have already been reported.[83, 84] Only one three-dimensional framework gallophosphate has been obtained with such cobalt complexes[85] and consists of a diamondlike network composed of tetrahedral $[GaO_4]$ units linked to $[PO_4]$ units. The complex remains intact during the reaction and is found trapped within the pores. Metallocene molecules, which were used in the synthesis of the large-pore zeolite, UTD-1, have also been used for the production of $AlPO_4$-5 and $AlPO_4$-16.[86] From these and other results, it has been shown that cobalt complexes are usually quite stable under hydrothermal conditions. However, similar experiments carried out with a tris(1,3 diaminopropane) nickel(II) complex[87] resulted in decomposition during hydrothermal treatment which led to the formation of a three-dimensional open-framework aluminophosphate with the ULM-3 structural type.

3.6. Methyl Phosphonates

Interest in open-framework aluminum phosphonates, as distinct from phosphates, was stimulated by the recent discovery of two microporous aluminum methylphosphonates, AlMePO-α and AlMePO-β, prepared by Maeda and co-workers.[88–90] These two structures, with the stoichiometry $Al_2(PO_3CH_3)$, are polymorphs and have unidimensional hexagonal channels composed of 18-rings. Aluminum is found in both tetrahedral and octahedral sites, and the methyl groups, which are covalently linked to the phosphorus atoms, protrude into the channels and reduce the pore size to around 6 Å. Layered aluminophosphonates have also been reported,[91] as expected by analogy with other areas of phosphonate chemistry.

3.7. Indium Phosphates

The aluminum and gallium phosphates confirm that it is possible to produce open three-dimensional architectures with metallic atoms in four-, five- or sixfold coordination. Indium, therefore, represents an interesting case since, by comparison with the smaller Al or Ga which can adopt three types of coordination, In is only expected to occur with octahedral coordination. This has been confirmed in several examples. In the first report of an organically templated indium phosphate, Haushalter[92] described a new open-framework material, $H_3NCH_2CH_2NH_3[In_2(HPO_4)_4]$, obtained with ethylenediamine. This work was followed by several other examples which incorporated various amine molecules,[93–95] including a pillared layer structure obtained with imidazole (Figure 12).[93] Other structures, analogous to known minerals, have been isolated: a hydrated indium phosphate, $InPO_4$-1,[96] related to the variscite type, and $InPO_4$-2,[97] related to the leucophosphite type. These compounds are characterized by small pores delimited by eight polyhedra.

In the presence of HF, three fluorinated indium phosphates have been obtained so far. One structure is lamellar[98] and is

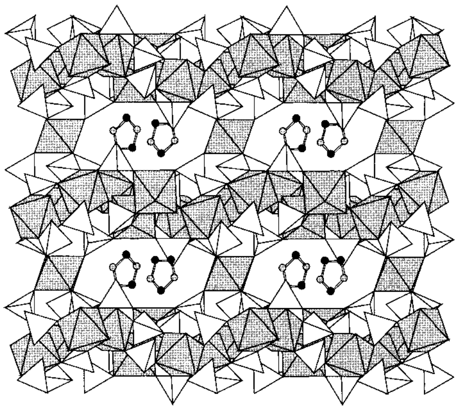

Figure 12. A view of the structure of imidazole-templated indium phosphate (see text). $[InO_6]$ octahedra are shown as shaded polyhedra.

isostructural with ULM-11 or $AlF(HPO_4)\cdot en$;[73] the second structure, $In_5(PO_4)_4F_3(H_2O)_2\cdot en_3$,[98] is three-dimensional with 10-ring channels which are spanned by ethylenediamine bridges between two opposite indium atoms. In both compounds, the nitrogen atoms of the template molecule are directly connected to indium atoms, and fluorine atoms are shared between indium atoms. A third phase, with the framework formula $[In_9(PO_4)_6(HPO_4)_2F_{16}]$,[99] is characterized by a high fluorine content. The three-dimensional network is composed of large elliptical cavities resulting from 14-ring channels adjacent to 8-ring channels. The fluorine atoms are found in either bridging or terminal positions.

3.8. Boron Phosphates

Surprisingly few studies have been reported the synthesis of microporous boron phosphates. From a crystal chemistry point of view, BPO_4 possesses the same dense structures as those of silica and $AlPO_4$,[100] and one might assume that it would be relatively easy to produce open-framework BPO_4 architectures. Boron is commonly found in trigonal or tetrahedral surroundings and it should be a good candidate for the preparation of solids based on (4;2)-connected networks, as in zeolites. It would seem that this is not the case. Boron has been incorporated to a small extent (less than 1 %) into the $AlPO_4$-5 framework,[101] where it substitutes for aluminum, but there are no reports to date of open-framework BPO_4 structures. However, a complex borophosphate has been described by Sevov;[102] this is a mixed cobalt–boron phosphate, $CoB_2P_3O_{12}(OH)\cdot C_2H_{10}N_2$ or BPO-1, in which the boron is found in tetrahedral coordination. The connection of the $[BO_4]$ units to $[PO_4]$ tetrahedra and $[CoO_6]$ octahedra by corner sharing generates 8-ring channels where the occluded ethylenediamine plays the role of the template.

3.9. New Open Frameworks in Metal-Containing AlPO and GaPO Materials

Interest in the incorporation of metal ions into the frameworks of aluminophosphates was initiated by researchers at Union Carbide with the discovery of the MAPO-*n* series (Section 3.1).[25] A number of new structural types have been found in this area, several of them having unique frameworks with no pure $AlPO_4$ analogue. For example, MAPO-36 (ATS)[2] can only be obtained in the presence of small amounts of a metal such as Mg, Mn, Zn, Co,[25] or Ti.[103] Other examples include magnesium-containing aluminophosphates such as DAF-1[104] or STA-*n*,[105] which have been prepared by the use of decathonium hydroxide and linear diquinuclidine, respectively, as templates. The structure of DAF-1 (DFO) possesses two parallel unidimensional channel systems containing puckered 12-rings in one case (ca. 6.1 Å) and planar 12-rings in the other (ca. 7.5 Å). It has been shown to be catalytically active for the acid-catalyzed conversion of isobutane to butenes and propene.[106] The structure of STA-1 (SAO) has large-pore channels delimited by 12-rings (ca. 6.6 Å and 7.2 Å) which run along two perpendicular directions, but without straight connections between them. In these compounds, the magnesium is partially substituted into the tetrahedrally coordinated aluminum framework sites. Chippindale and co-workers have described several examples of mixed cobalt(II)–gallium phosphates, some of which are analogous to known zeolites. For example, $(C_5H_5NH)[CoGa_2(PO_4)_3]$[107] and $(C_4NH_{10})[CoGa(PO_4)_2]$[108] have the LAU and GIS framework topologies, respectively. The laumontite structure type has also been obtained with iron or manganese replacing cobalt atoms in the framework.[109] By contrast, CoGaPO-5 (CGF)[110] exhibits a novel framework topology based on alternating $[PO_4]$ and $[MO_4]$ (M = Ga, Co) tetrahedra. It consists of two sets of channels delimited by 8- and 10-rings perpendicular to 8-ring channels, similar to the system encountered in heulandite.[2]

Very recently, Stucky and co-workers[111, 112] reported an extensive study of microporous cobalt–aluminum and cobalt–gallium phosphates materials, of general formula $(R)Co_xM_{1-x}PO_4$ (R = organic template, M = Al, Ga). This study was based on the concept of template–framework charge matching, rather than the steric hindrance of the structure-directing agent: the negative charge of the framework, which depends on the Co^{2+}/M^{3+} ratio, is counterbalanced by the positive charge of the organic species. By varying the organic charge/volume ratio, cobalt can be incorporated more or less extensively into the framework. Several zeolite analogues were synthesized, as well as new frameworks that had been predicted previously. For example, the compound ACP-1 (ACO), which has a structure built up from the connection of D4R cages to form three-dimensional 8-ring channels, has not yet been observed in aluminosilicates. This work was then extended to other divalent cations, such as Mg^{2+}, Zn^{2+}, and Mn^{2+}, and several materials designated UCSB-*n*, were obtained, three with frameworks characterized by multidimensional 12-ring channels. UCSB-10 (SBT) and UCSB-6 (SBS) exhibit three-dimensional 12-ring channel systems and their structures, built up from cancrinite-like cages, are related to that of faujasite (FAU) and its hexagonal polymorph (EMT). In this description, the sodalite cages of FAU and EMT types are replaced by cancrinite cages. These frameworks differ in the packing of the cancrinite cages, and large cavities bounded by three, four, or five 12-rings are produced. The architecture of UCSB-8 (SBE) consists of two sets of perpendicular 12-ring channels interconnected with 8-ring channels. At the intersection, this results in large cavities bounded by 64 T atoms (four 12-rings and two 8-rings).

In all the above phases, the metal is incorporated into the network in a tetrahedral site. However, there are a few examples where cobalt adopts octahedral coordination, as in the ammonium cobalt–gallium phosphate $NH_4[CoGa_2(PO_4)_3(H_2O)_2]$[113] and the cobalt–aluminum phosphate $CoAl(PO_4)_2 \cdot en$.[114] In the latter, the coordination of the cobalt atom is completed by five oxygen atoms and one nitrogen atom of the ethylenediamine. In the manganese–gallium phosphate, $(C_6N_2H_{14})[MnGa(HPO_4)(PO_4)]$ or MnGaPO-2,[115] the manganese ion is in a five-coordinated site with square-pyramidal geometry.

4. Other Main Block Open Frameworks

4.1. Beryllium and Zinc Compounds

In addition to the study of novel open frameworks with metals substituting into zeolites, aluminophosphates and so on, there have been numerous recent publications concerning the synthesis of open frameworks which contain exclusively metallic ions in combination with phosphate. In much of this work, the strategy has been to choose elements that can adopt tetrahedral coordination in the solid state. At the beginning of the 1990s, the groups of Meier[116] and Stucky[117] described the synthesis of beryllo- and zincophosphates and arsenates, denoted as BePO, ZnPO, BeAsO and ZnAsO. Most of these compounds were prepared under hydrothermal conditions, although some of them were obtained from milder reactions at temperatures ranging from -20 to 70 °C. Their structures consist of vertex-sharing networks of $[MO_4]$ ($M = Zn^{2+}, Be^{2+}$) and $[XO_4]$ ($X = P$, As) tetrahedra, corresponding to anionic frameworks, $[MXO_4^-]$, that are equivalent to those encountered in aluminosilicates of composition $[AlSiO_4^-]$. By the use of alkaline cations for charge compensation, several zeolite analogs have been obtained, for example ZnPO, ZnAsO, BePO, and BeAsO sodalites,[118, 119] ZnPO and BePO faujasites,[120] BePO and BeAsO RHO,[121] and the ZnPO, ZnAsO, BePO, and BeAsO ABW.[117, 122] New topologies were also found, including the beryllophosphate $Na_{0.5}K_{0.5}BePO_4$ (BPH),[123] the chiral framework, $NaZnPO_4 \cdot H_2O$ (CZP),[124] and the $A_3Zn_4O(XO_4)_3 \cdot n H_2O$ (A = alkaline, X = P, As) series[125] in which both Zn-O-P and Zn-O-Zn linkages occur.

Certain of the zincophosphates contain tetrahedral units with terminal hydroxy groups (HPO_4^{2-} or/and $H_2PO_4^-$), thereby limiting the connection of these units to other $[MO_4]$ tetrahedra. Consequently, several three-dimensional topologies with interrupted networks have been prepared.[126–132] With the exception of $H[Zn_4(PO_4)_3] \cdot H_2O$ and $(NH(CH_3)_3)[Zn_4(H_2O)(PO_4)_3]$,[132] the Zn/P ratio in these compounds is very often less than 1. A higher Zn content implies some Zn-O-Zn linkages, the bridging oxygen atom being in trigonal coordination with a link to a phosphorus atom. This is a situation where metal-oxygen-metal connectivities occur with the metal in tetrahedral surroundings. This is not usually observed in aluminosilicates, nor in AlPOs unless the coordination of aluminum is increased to five or six. More recently, Harrison and Phillips[133, 134] have described the synthesis of a series of zincophosphates prepared with the nitrogen-rich guanidinium cation; a molecule with trigonal planar geometry. Despite the small size of this organic species, the open frameworks of these compounds exhibits large pores bounded by 12-ring[134] or 18-ring channels.[133] Although the Zn/P ratio is greater than 1, there is no Zn-O-Zn bonding in this structure; only terminal $Zn-OH_2$ bonds occur, as was also observed in the zincophosphate templated by the DABCO molecule.[127] In $N(CH_3)_4[ZnH_3(PO_4)_2]$,[135] the three-dimensional network contains 12-ring channels but the tetrahedral framework is characterized by one of the lowest framework densities observed so far for a microporous compound (10.1 T atoms/1000 Å^3). A mixed zinc–aluminum phosphate, denoted ZAPO-M1 (ZON),[136] has also been reported and is isostructural with the fluorinated aluminophosphate UiO-7.[82] Other zinc derivatives, including a zincoborate[137] and a zincocarbonate,[138] have also been mentioned and present alternatives systems for the elaboration of open frameworks.

Another feature of beryllium and zinc phosphate chemistry is the formation of topologies which contain 3-ring units as a basic building block. This feature is observed, for example, in the beryllosilicate mineral, lovdarite.[2] Brunner and Meier[139] found a linear correlation between the occurrence of small ring sizes and the framework density. From Brunner and Meier's concept, one strategy to obtain materials with low framework density is to synthesize beryllium- and zinc-based materials, but, due the toxicity of the beryllium, efforts concentrated mainly on the study of the zinc compounds. Several new topologies based on three-membered ring units have thus been reported: VPI-7 (VSV),[10] VPI-9 (VNI), and RUB-17 (RSN).[140]

4.2. Borates and Germanates

Although open-framework borosilicates (Section 2) and borophosphates (Section 3.8) have attracted a certain amount of attention, many other borate systems still remain to be explored. In the light of the enormous literature on condensed borates, this surely represents an interesting opportunity for future research. One interesting family that has been reported is the boron sodalites, such as $Zn_4O(BO_2)_6$.[141] These comprise a framework based exclusively upon tetrahedral $[BO_4]$ units, the zinc atoms being located in extra-framework cation positions.

Equally surprisingly, open-framework structures based upon germanates have not been extensively studied in comparison with the huge effort that has been expended on silicates and phosphates. However, one versatile family of composition $M_{4-x}H_xGe_7O_{16} \cdot n H_2O$ has been known for many years[142] and several structural variants are known.[143–145] The framework structure of these materials is composed of a central cluster of four face- and edge-sharing $[GeO_6]$ octahedra; these clusters are linked to each other through $[GeO_4]$

tetrahedra. This coordination behavior is consistent with the larger size of germanium compared to silicon. These germanates are reported to exhibit useful ion-exchange behavior and ionic conductivity,[146] but we are not aware of any work relating to other properties.

A quite different germanate architecture has been described recently by Cascales et al.[147] As with the system discussed above, $(NH_4)_2Ge_7O_{15}$ contains both tetrahedral and octahedral $[GeO_n]$ units, but their connectivities are quite different, and give rise to a rare example of a 9-ring window. Given the occurrence of both tetrahedral and octahedral coordination with germanium, it could be of great interest to explore mixed Si,Ge systems. Similarly, recent work on the gallium- and aluminum-containing germanate frameworks, UCBS-9 and UCSB-11,[148] has revealed a tendency for the formation of 3-ring units, as is also found in certain beryllium- and zinc-containing systems (Section 4.1).

4.3. Tin(II) Phosphates

Very recently, some open-framework tin(II) phosphates templated with organic molecules have been prepared by Cheetham and Natarajan.[149–151] Since tin in the 2+ oxidation state is associated with a lone pair of electrons, its presence in the structure results in unique building units for open frameworks. Tin(II) is mainly found in threefold coordination, connected to three phosphorus atoms by bridging oxygens located at the vertices of a trigonal pyramid (Figure 13). The lone pair occupies the fourth vertex of a hypothetical tetrahedron. For three-dimensional systems based on the alternation of $[PO_4]$ tetrahedra and $[SnO_3]$ trigonal pyramids,[149, 150] this yields a framework of general formula $[Sn_4P_3O_{12}^-]$ with pores in which the organic amine species are occluded. The channels found to date include both 8- and 12-rings, but the effective size for accessibility is smaller than anticipated due to the hindrance of the lone pair of electrons that point towards the centers of the channels. In the oxophosphate phase, SnOPO-1,[151] the Sn/P ratio is 2 and tin atoms are connected together by a common oxygen atom which coordinates three tin atoms. The three-dimensional framework encapsulates ammonium cations and star-shaped 10-ring channels are generated. In a system with a Sn/P ratio of 3/2, the presence of both trigonal-pyramidal $[SnO_3]$ and square-pyramidal $[SnO_4]$ units also results in Sn-O-Sn linkages.[152] As in the AlPO systems, monomeric,[153] chain,[154] layered[155] and three-dimensional chiral[156] structures have also been observed, and there is evidence that a simple tetramer, $[Sn_2P_2O_8]$, may be a fundamental building unit in many of these structures.

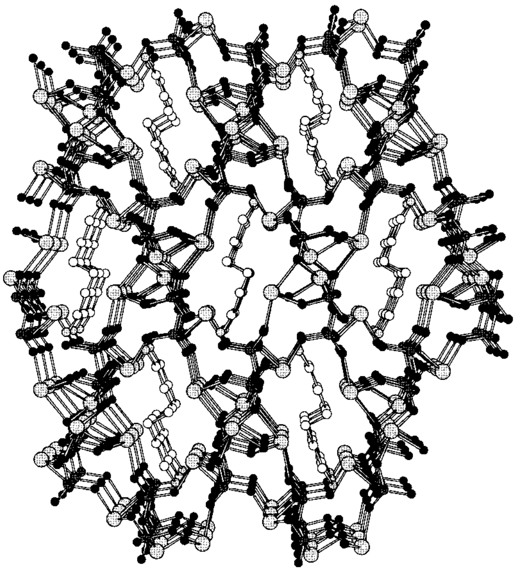

Figure 13. A perspective view of the structure of a Sn^{II} phosphate, with 1,6-diaminohexane in the channels (Sn: large shaded spheres; P: medium shaded spheres; O: small black spheres; C: small white spheres; N: small shaded spheres). Note that the lone pairs on tin(II) point into the channels.

5. Transition Metal Phosphates

Following the successful introduction of transition metals into the zeolitic AlPOs and GaPOs and the discovery of open-framework solids with coordinations numbers larger than four, several groups attempted to synthesize phosphates containing exclusively transition metals. Such materials offer a great deal of scope, since they may contain metals in different valence states and/or different coordination numbers, and the anionic framework may be all oxide or oxide and fluoride. The presentation will follow a chronological sequence.

5.1. Molybdenum Phosphates

Several years after the discovery of $MoOPO_4$ by Kierkegaard and Westerlund,[157] the reduced molybdenum phosphates were studied simultaneously by the Raveau and Haushalter groups.[158, 159] They initially focused on solid-state synthesis techniques at temperatures above 750 °C, the reaction mixture being alkali metal phosphate or MoO_3, a phosphate source (P_2O_5 or metal phosphate) and Mo metal, which were heated together in an evacuated quartz ampoule. The resulting molybdenum phosphates had a Mo/P ratio lower than 1.

In this series of high-temperature materials, inorganic cations are accommodated into condensed frameworks with various topologies. Costentin et al. proposed[158] a classification of these phases according to the connectivity of the molybdenum polyhedra. Class I involves structures in which the $[MoO_6]$ octahedra are isolated from each other, which means they share five of their corners with $[PO_4]$ tetrahedra, the sixth oxygen, corresponding to the very short Mo=O bond, being terminal. This family, the largest in the series, mainly corresponds to Mo/P ratios of 1/2 and 2/3, and gives rise to many different topologies, principally with $[Mo_2P_3O_{13}]_\infty$ frameworks. Class II is characterized by infinite $[MoO_{6/2}]_\infty$ octahedral chains in which short Mo–O bonds (≈ 1.65 Å) alternate with long bonds (≈ 2.5 Å) along the axes of the chains. This second family does not exhibit any free apices;

the four available apices are shared with [PO_4] tetrahedra. The typical structure of this class is $MoOPO_4$.[157] An interesting example that combines class I and class II is $AgMo_5P_8O_{33}$[160] which gives rise to 10- and 8-rings, the latter containing the Ag^+ ions (Figure 14). Class III has a few representatives with Mo/P < 1. It concerns structures that exhibit units with a limited number of molybdenum octahedra, for example in $K_2Mo_2P_2O_{11}$ where the framework is built from corner-sharing [$Mo_2P_2O_{15}$] tetramers. In the latter, two Mo octahedra share a vertex, and two tetrahedra are grafted on to the Mo dimer by corner sharing. An increase of the Mo/P ratio implies a further condensation of the Mo octahedra and leads to structures in which these polyhedra share edges and faces. The building units which describe the frameworks are often octameric, with four Mo and four P atoms arranged in three different ways. This was first observed by Haushalter[159] in $Cs_3Mo_4P_3O_{16}$, which is isotypic with the mineral pharmacosiderite;[161] it contains octameric [Mo_4P_4] clusters linked by corners. These clusters comprise a central tetramer of MoO_6 octahedra, each of them sharing three edges with the others; six phosphate groups cap the Mo tetramer by shared corners.

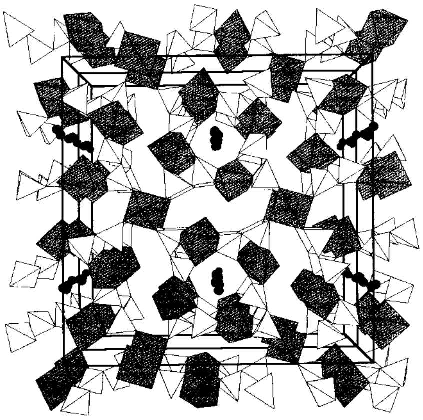

Figure 14. A perspective view of the structure of $AgMo_5P_8O_{33}$ (Ag: small spheres; [MoO_6] polyhedra are dark shaded; [PO_4] tetrahedra are light shaded)

All of these high-temperature MoPOs show very poor ion-exchange properties. In order to form materials with significant internal micropore volume, it is necessary to use hydrothermal techniques and to try to incorporate large removable cations. With this approach, Haushalter et al.[159] successfully prepared some MoPOs with open frameworks by allowing a molybdenum source (MoO_3+Mo or $MoCl_5$) to react with phosphoric acid and an organic cationic template in an autoclave in the temperature range 200–400 °C. The first MoPO, $(Me_4N)_{1.3}(H_30)_{0.7}[Mo_4O_8(PO_4)_2]\cdot 2H_2O$,[162] is built up from another type of tetramer, close to that of pharmacosiderite, with the same central tetramer of Mo octahedra, but with only four phosphate groups. Such a cluster can present different connectivities to form various frameworks that lead to different pore openings and different cavity diameters (2.8–7 Å). Several other open-framework solids were also synthesized in this way by changing the nature of the template; they contain a third form of octameric unit, already described in leucophosphite[162] and spheniscidite,[163] in which the central tetramer is composed of two edge-sharing octahedra on the edge of which are grafted two other octahedra over shared corners. Finally, another open-framework topology was obtained when a mixture of organic and inorganic cations is used during the synthesis. It derives from the $MoOPO_4$ structure in the sense that the bridging oxygen atoms between two layers are replaced by phosphate groups.[164]

5.2. Vanadium Phosphates

Interest in this family of materials stemmed initially from the catalytic applications of vanadyl pyrophosphate $(VO)_2P_2O_7$ in the selective oxidation of butane to maleic anhydride.[165, 166] As with the MoPOs described above, the VPOs were synthesized by the use of both high-temperature solid-state reactions with inorganic cations and low-temperature hydrothermal techniques with amines as templates. The association of different vanadium valence states (V, IV, III) with their various polyhedra (tetrahedra, square pyramids, distorted and regular octahedra) leads to a very large diversity for the resulting structures. For the solid-state approach, which will not be described in detail here, the major contributors were the groups of Haushalter and Jacobson in USA, Raveau in France, Lii in Taiwan, and Beltran-Porter in Spain. A good list of references to the corresponding works can be found in ref. [167]. As with the condensed molybdenum phosphates, several situations occur for the vanadium subnetwork: isolated polyhedra and corner- and edge-sharing chains (these are connected to each other by [PO_4] tetrahedra, but their connections always leave small tunnels inside which cationic exchange is difficult).

The success obtained with MoPOs with hydrothermal techniques and organic templates led Haushalter[168] and Férey[169] to investigate the corresponding V-P-O systems. Two eye-catching results originate from this research: a) the first evidence of an inorganic double helix in $[(CH_3)_2NH_2]K_4[V_{10}O_{10}(H_2O)_2(OH)_4(PO_4)_7]\cdot 4H_2O$[168] and b) the existence of giant voids in the two square-pyramidal–tetrahedral framework vanadium phosphates $Cs_3[V_5O_9(PO_4)_2]\cdot xH_2O$ and $[HN(CH_2\text{-}CH_2)_3NH]K_{1.35}[V_5O_9(PO_4)_2]\cdot xH_2O$.[170] In the double-helix compound, the structure is built up from two crystallographically independent V_5P_4 enneamers. These oligomers can be described as a linear trimer of *trans* corner-sharing octahedra in which long and short V=O bonds alternate along the axis of the chain. Each of the two outer octahedra of the trimer share one edge perpendicular to the axis of the trimer with a square pyramid, thus forming pentameric building units. The four [PO_4] tetrahedra share two of their oxygen atoms with those of the basal plane of each octahedron of the trimer. These pentamers are arranged so as to form spirals, with four pentamers per spiral of unit cell length along [001]. These spirals are intertwined to give the two strands of a double helix. Some of the remaining phosphate groups connect the strands to one another, and others bond one double helix to another. The strands and double helices intergrow with each another in an extremely complicated manner. This arrangement generates different cavities in which K^+ and protonated dimethylamines are inserted. The K^+ ions lie in the more polar regions of the cavities and are solvated by water. At very low temperatures (<2.5 K), the solid exhibits antiferromagnetic properties.

The structures of $Cs_3[V_5O_9(PO_4)_2] \cdot x H_2O$ and its homologue with DABCO and potassium (Figure 15)[170] are characterized by a very unusual pentameric unit of square-pyramidal coordinated vanadium atoms $[V_5O_9(PO_4)_{4/2}]$, in the shape of a spiked helmet; the V_5 pentamers consist of a central $[VO_5]$ square pyramid which shares its four basal edges with those of the four satellite square-pyramidal vanadium centers. The four phosphate tetrahedra each link two satellites by corners. Such an arrangement was already encountered in molecular chemistry with the famous vanadium clusters described by Müller.[171] The curvature of these pentamers explains the formation of very large cavities. Each cavity, which could contain a sphere of ca. 13 Å diameter, is occupied by 12 DABCO molecules, 32 K^+ cations and some water of crystallization. At its maximum diameter, it displays an enormous 32-ring window and connects over 16-ring windows with the other supercages. These materials possess one of the lowest framework densities (9.3 metal atoms/1000 $Å^3$) and the largest cavities observed so far in open-framework materials.

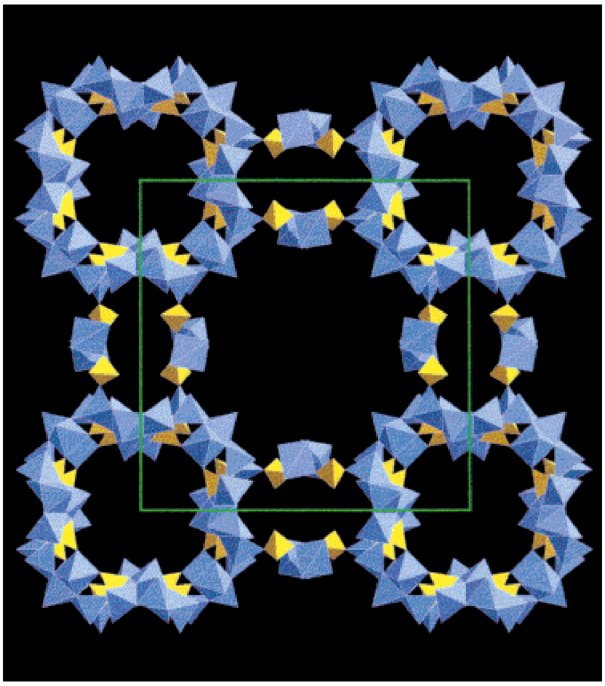

Figure 15. A view of the open framework of $Cs_3[V_5O_9(PO_4)_2] \cdot x H_2O$. The Cs and H_2O are not shown.

Beside these two original compounds, a mixed-valence material must also be mentioned owing to its very interesting structure: $(H_2en)_3[V^{III}(H_2O)_2(V^{IV}O)_8(OH)_4(HPO_4)_4(PO_4)_4(H_2O)_2] \cdot 2H_2O$. It may be described[172] as undulating layers constructed of corner-sharing V^{IV} square pyramids and phosphate tetrahedra; these layers are then connected by single $[V^{III}(H_2O)_2]$ centers to form a framework which exhibits elliptical channels (ca. 7 × 18 Å). Furthermore Beltran-Porter et al. showed that it was possible to substitute V^{III} by Fe^{III} in this structure type.[173]

All of the above compounds are oxides. The application of the fluoride route already described (Section 3.4) for $AlPO_4$s and $GaPO_4$s has showed that it is also possible to obtain open-framework structures containing fluoride. This led to the discovery by Riou and Férey[174] of the first open-framework vanado(v)fluorophosphate, ULM-7 or $(H_3N(CH_2\text{-}CH_2)NH_3)[(V^vO_2)_2(PO_4)F]$, in which the building units are V_2P trimers. Vanadium exhibits both octahedral and square-pyramidal coordination, and a fluoride ion, which belongs to both polyhedra, is shared between them. Each V polyhedron shares an oxygen with the phosphate group of the trimer. The three-dimensional network generated by corner sharing of these trimers exhibits 10-rings in which diprotonated amines are inserted. Two new vanadofluorophosphates have recently been reported;[167] one is mixed valence V^{III}/V^{IV} while the other contains only V^{IV}.

5.3. Iron Phosphates

In the mineral kingdom, iron phosphates are among the most important materials besides silicates and aluminates. Many phases, with a large number of both open and dense octahedral–tetrahedral frameworks, have been described in the Fe-P-O and the M-Fe-P-O (M = alkaline; alkaline-earth) systems.[175, 176] The most striking example of an open-framework iron phosphate is provided by the mineral cacoxenite,[177] $[AlFe_{24}(OH)_{12}(PO_4)_{17}(H_2O)_{24}] \cdot 51H_2O$, (Figure 16) which contains cylindrical tunnels occupied by water molecules, with a free diameter of 14.2 Å. The first synthetic materials, analogues of the minerals hureaulite and alluaudite, were described by Corbin et al. in 1986[178] and opened the way for synthetic open-framework iron phosphates whose applications in catalysis could be very important. For example, dense

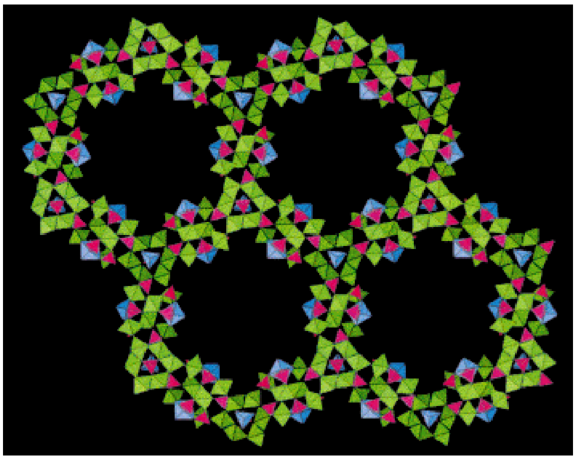

Figure 16. A view of the structure of the mineral cacoxenite showing the channels running along the *c* axis. The relative size of this Figure is 1.5 times smaller than for the remaining Figures. Unfortunately, the framework collapses on dehydration.

iron phosphates are used as selective catalysts during the oxidative dehydrogenation of isobutyric acid into methacrylic acid.

Paradoxically, and at variance with the other families, the first synthetic, open-framework iron phosphates containing organic cations in the pores were not pure oxides, but oxide–fluorides obtained by the use of the fluoride route already described. Indeed, the hypothesis for the formation of the ULM solids proposed by Férey[73] advanced the possibility of obtaining hitherto unknown iron phosphates with open frameworks. The first of them, ULM-12 or $N_2C_6H_{14}[Fe_4(PO_4)_4(H_2O)_3F_2]$, was discovered in 1996.[179] Other oxyfluorinated compounds followed, but the first all-oxide homologues were synthesized in 1997 in the group of Lii in Taiwan.[180] A complete description of these oxidic phases is given elsewhere[180] and will not be discussed here. However, we would like to draw attention to the building units that often appear in these phases. Whereas the majority of the units which appear in the ULM series (fluorinated medium) are M_3P_3 hexamers, when fluorine is absent from the synthesis most of them are M_4P_4 octamers. Moreover, these octamers are very close to the D4R cages encountered in cloverite and LTA, with a central oxygen replacing fluorine in the cages. The following section will be devoted to the Fe-ULM series.

From the chemical point of view, all the ULM phases in the system Fe-P-O-F-amine have very slow kinetics of formation, and many intermediate phases appear before those corresponding to thermodynamic equilibrium are formed. As a function of pH, temperature, and concentration, the resulting compounds are either pure Fe^{III} or mixed-valence Fe^{II}/Fe^{III} solids. Among the ten phases already characterized, many are iron analogues of gallium compounds. However, three of them are of particular interest. In ULM-12, which was already introduced above, the three-dimensional structure (Figure 17) arises from the corner sharing of two types of building blocks, one a hexamer with Fe–F–Fe–F–Fe bonds, similar to those encountered in the Ga-ULM series (Section 3.4), and one a dimer corresponding to the monophosphate aqua complex of iron. In the hexamer, two of the three iron ions are octahedrally, including a water molecule in the coordination, while in the dimer, a square-pyramidal coordination of Fe is observed with just one aqua ligand. The corner-sharing assembly of these oligomers defines 8-ring channels in which DABCO ions are housed. The irreversible dehydration of ULM-12 yields ULM-19, whose structure is close to that of ULM-12 and corresponds to the loss of the water molecules that were in the coordination polyhedra. This leads to a drastic change in the nature of the polyhedra since the structure of ULM-19 exhibits one iron octahedron, two trigonal bipyramids and one tetrahedron instead of three octahedra and one square pyramid.

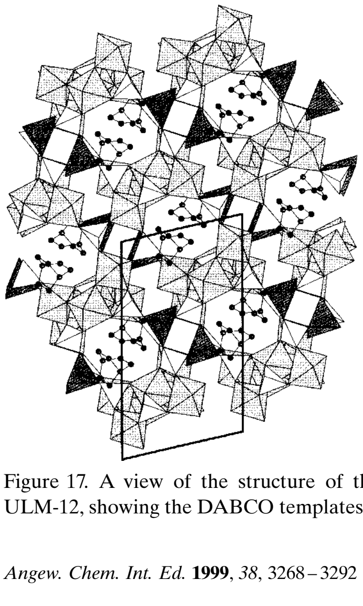

Figure 17. A view of the structure of the fluorinated ferric phosphate, ULM-12, showing the DABCO templates encapsulated in the 8-ring cages.

ULM-15 (Figure 18) obtained with 1,3-diaminopropane,[181] has a singular structure built up from dimers and infinite *trans* chains of Fe^{III} octahedra linked by phosphate groups to form corrugated planes. The three-dimensional character is provided by single tetrahedra which link two consecutive planes, and leads to 16-ring ovoid windows with dimensions of ca. 12 × 7 Å.

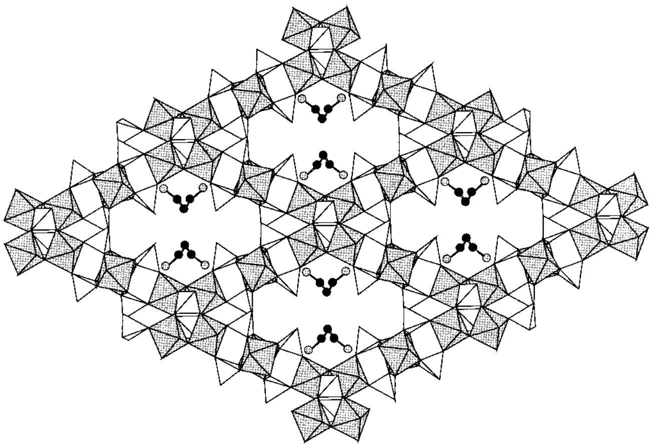

Figure 18. A view of the structure of the fluorinated iron phosphate, ULM-15, templated by ethylenediamine.

The main interest in these ferrofluorophosphates concerns their magnetic properties. Despite the existence of isolated clusters linked by phosphate groups, three-dimensional magnetic ordering takes place in the range 15–40 K, with either antiferro- or ferrimagnetic properties. They open the way to a new class of open-framework solids that combine the well-known sieving properties with magnetic properties; these might be used for magnetic separation if the ordering temperatures reached are sufficiently high.

5.4. Cobalt(II) and Manganese Phosphates

Cobalt(II) has a special place in the open-framework family because it is one of the few transition metal cations that easily exhibits tetrahedral coordination in addition to five- and sixfold coordination. Moreover, magnetic coupling can give rise to interesting magnetic properties, similar to those described above for iron. Finally, it is well known that Co^{2+} doping enhances the catalytic performance of certain zeolites and related compounds. This property has led[182, 111] to many reports of Co^{2+}-doped alumino-, gallo-, and zincophosphates. For instance, CoAPO-5 and CoAPO-11 have been used for the autoxidation of cyclohexane[183] and *p*-cresol.[184]

Recently, a substantial effort was made to synthesize pure cobalt phosphates with an open framework with either inorganic or organic templates. The first success[185] concerned the pseudo tetragonal three-dimensional material $CoPO_4 \cdot 0.5\,C_2H_{10}N_2$. The framework consists of three systems of channels with 8-ring windows limited by Co and P tetrahedra in strict alternation. The dimensions are 3.9 × 4.7 Å, and the compound becomes antiferromagnetic at 2 K. The three-dimensional character exists only with ethylenediamine. As soon as the length of the carbon chain increases (e.g. 1,3-diaminopropane and 1,4-diaminobutane), the solids become two-dimensional[186] with planes built up from corner-sharing *trans* chains of Co^{2+} tetrahedra linked by phosphate groups.

One of the main contributions to the CoPOs has been made by Stucky's group.[187] Being aware that the tremendous success with the aluminophosphate system was in part due to the initial recognition of structural analogies between $AlPO_4$ and SiO_4, they sought to determine if the same analogies also exist between cobalt phosphates and aluminosilicate minerals. This design approach led them to characterize, with alkali metal (M = Na, K, Rb) and NH_4^+ ions, chiral tetrahedral $MCoPO_4$ cobalt phosphates. These exhibit either the zeolite Li-ABW structure type[2] with NH_4^+ and Rb^+, or a hexagonal structure, intermediate between the ABW and tridymite structures, with Na^+, K^+, and NH_4^+ cations. The latter contains 6-ring channels. This paper clearly indicates the difficulty of the corresponding chemistry and underlines the drastic influence of pH and the nature of the solvent on the synthesis of the desired products. Despite the usually antiferromagnetic behavior of these $CoPO_4$ materials, the sodium compound is ferromagnetic at 2 K.

Manganese phosphates with an open framework are very scarce. The chemistry of new phases in this area is emerging with some recent attempts by Kaucic et al.[188] and Rziha et al.[189] In the case of nickel phosphates there is again little to report, though we have recently discovered a large-pore nickel phosphate (VSB-1 (Versailles/Santa Barbara-1)) which has very interesting sorption and magnetic properties.[190] Further work is clearly merited in these and other systems such as chromium and copper phosphates.

5.5. Zirconium and Titanium Phosphates

With tetravalent cations, synthesis often leads to two-dimensional phosphates, as is clearly shown by the work of Clearfield on the zirconium phosphates.[191] However, the fluoride route has very recently led to the first zirconium phosphates with three-dimensional open-framework structures.[192, 193] For example, $[(enH_2)_{0.5}][Zr_2(PO_4)_2(HPO_4)F] \cdot H_2O$ exhibits 8-ring tunnels formed by strict Zr–P alternation. The Zr octahedra are of two types: ZrO_6 and ZrO_5F, the Zr–F bond being terminal.

The same method, applied to titanium, very recently led[194] to a mixed-valence fluorinated titanium phosphate with 7-ring channels. In non-fluorinated medium, a new phosphate, ρ-TiP, has been also found,[195] with three types of tunnels (4-, 6-, 8-rings).

6. Chalcogenides, Halides, and Nitrides

6.1. Sulfides and Selenides

The known classes of open-framework materials are overwhelmingly dominated by oxide or mixed oxide/fluoride matrices. In 1989, however, Bedard and co-workers of UOP[196] proposed to extend this class of materials to metal sulfide compounds. Metals and semimetals exhibiting tetrahedral coordination in sulfides were considered first in order to imitate the crystal chemistry of the microporous zeolites and aluminophosphates. In the original paper, only germanium(IV) and tin(IV) sulfides were described, but the preparation of antimony(III)[197] and indium(III)[198] sulfides was subsequently reported by Parise. A new nomenclature was adopted corresponding to the generic name R-M′MS-*n*, where R indicates the organic template, M′ is a 3d (or 4d) metal, M represents germanium (noted G), tin (Sn), antimony (Sb) or indium (In) and n corresponds to a structural type. These compounds are obtained under hydrothermal conditions in a similar way to zeolites and other derivatives. The reaction is carried out with a mixture of metal sulfide (or metal + sulfur) and an amine or quaternary alkylammonium species which is heated at temperatures from 25 to 180 °C for several days. In some preparations, the organic template is used in the carbonate or hydrogenosulfide (HS^-) form, rather than the hydroxide; this appears to give rise to a mineralizer effect. By changing the nature of the organic species, new open frameworks have been isolated and different configurations of building units have been observed, depending on the elements (Ge, Sn, Sb, or In).

The reaction of germanium sulfide with organic amines frequently leads to the formation of amine germanium sulfides which contain clusters of $[Ge_4S_{10}]^{4-}$ which may be found isolated or in low-dimensional compounds such as DPA-GS-8.[199] This kind of tetrameric unit is quite common in germanium sulfide chemistry and is related to the structure of adamantane (Figure 19). The four germanium atoms are tetrahedrally coordinated by sulfur atoms and are connected by shared corners. This unit can be viewed as a tetrahedron in which germanium occupies each corner and is reminiscent of the tetrahedral units $[SiO_4]^{4-}$ observed in silicates. The formation of three-dimensional networks is achieved by the use of a metal that furnishes the connection between the $[Ge_4S_{10}]$ adamantane units. The utilization of several metals, including Mn, Fe, Co, Ni, Cu, Zn, and Ga,[196, 200] has been reported.

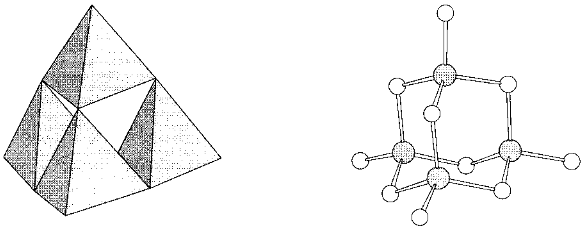

Figure 19. Tetrahedral basic building unit $[Ge_4S_{10}]^{4-}$ usually described in the microporous germanium sulfides. Ge: large grey spheres, S: small white spheres.

Yaghi and co-workers[201] have proposed an alternative route for the synthesis of these sulfides. They were able to obtain crystals from the diffusion of an aqueous solution of the 3d metal into a solution of an amine – $[Ge_4S_{10}]$ complex at room temperature. In the case of copper(I), the $[Ge_4S_{10}]$ tetrahedral clusters are bridged by the Cu^I cations which can be in linear twofold coordination ($[CuS_2]$)[202] or trigonal planar threefold coordination ($[CuS_3]$).[203] An example of metal – metal linking is found in the mixed silver – copper germanium sulfide, $(CH_3)_4N[(Ag_2,Cu_2)Ge_4S_{10}]$.[204] The open framework is built up from the connection of the $[Ge_4S_{10}]$ unit by metal – metal bonds of the type $[Ge(\mu\text{-}S)]_2M\text{-}M[Ge(\mu\text{-}S)]_2$ ($M = Cu$, Ag). New topologies have been discovered with very low framework densities. For instance, the structure of the M′GS-2 type is composed of puckered 12-ring channels which contain organic species and has a framework density of 7.27 T/1000 Å^3, which is much less than that encountered in oxide frameworks (e.g. 12.7 T/1000 Å^3 for the FAU type). For some frameworks, the arrangement of the tetrahedral $[Ge_4S_{10}]$ units resembles that occurring in the diamond[201, 202] or blende[204] types. With manganese, a germanium sulfide[205] has been obtained with a structure analogous to that of zeolite Li-ABW (Figure 20).

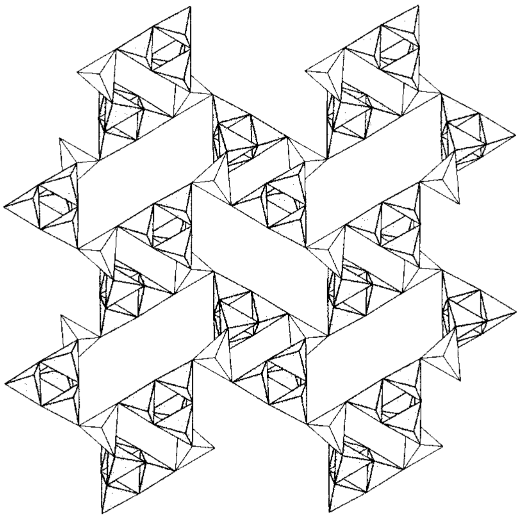

Figure 20. Representation of the open framework of $MnGe_4S_{10} \cdot C_6H_{14}N_2 \cdot 3H_2O$ analogous to zeolite Li-A(BOW). Manganese polyhedra, $[MnS_4]$, are indicated by white tetrahedra, germanium polyhedra, $[GeS_4]$, are indicated by gray tetrahedra. Amines have been omitted for clarity.

Very few compounds with three-dimensional open frameworks have been prepared with tin chalcogenides. The structures of the pure tin sulfides are most often lamellar and several studies have been reported on the structure types R-SnS-1[196, 206, 207] and R-SnS-3,[207–209] with $[Sn_3S_7]^{2-}$ and $[Sn_4S_9]^{2-}$ network compositions, respectively. The R-SnS-1 structure type can also be obtained with selenium instead of sulfur.[210] The inorganic layers of these compounds are composed of $[Sn_3S_4]$ broken-cube building units linked together by double-bridging $Sn(\mu\text{-}S)_2Sn$ sulfur bonds (Figure 21). The resulting polyhedral coordination for tin corresponds to trigonal bipyramid SnS_5 instead of the tetrahedral geometry of the germanium compounds. The layer contains hexagonal 12-ring apertures for R-SnS-1 (Figure 22) and elliptical 16-ring apertures in R-SnS-3. In the latter compound, the tin atoms are in fourfold (tetrahedral) and fivefold (trigonal bipyramid) coordination, whereas they are in fivefold coordination exclusively in R-SnS-1. Studies have been undertaken concerning the mechanism of the formation of these two phases.[211] Three types of intermediates have been isolated during the condensation process and it is thought that the framework may be formed from the dimeric precursor $[Sn_2S_6]^{4-}$, which is in solution. Another layered phase of composition $[Sn_5S_{12}]^{4-}$ has also been mentioned by Parise.[212] The situation for tin is different since it is found in both five- and sixfold coordination in a layer that consists of edge-linked tin polyhedra.

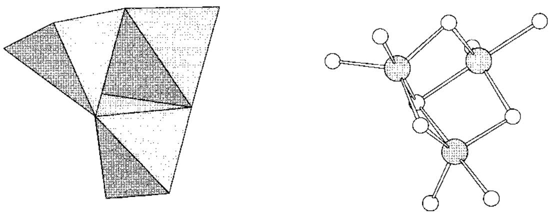

Figure 21. Representation of the broken cube cluster, Sn_3S_4, for R-SnS-1. Sn: large grey spheres, S: small white spheres.

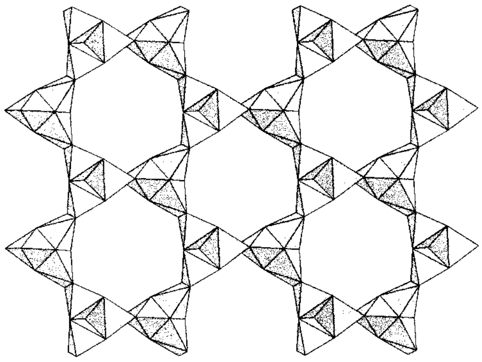

Figure 22. A view of the inorganic layer of R-SnS-1.

In contrast to the tin sulfides, a three-dimensional framework has been found with a tin oxysulfide.[213] The structure is built up from clusters of composition $[Sn_{10}S_{20}O_4]^{8-}$ connected by sulfur bridges (Figure 23). This unit can be described as a super tetrahedron composed of four $[Sn_4]$ tetrahedra. Each node of the four tetrahedra is occupied by one tin atom. The tin atoms are coordinated by one oxygen atom and four sulfur

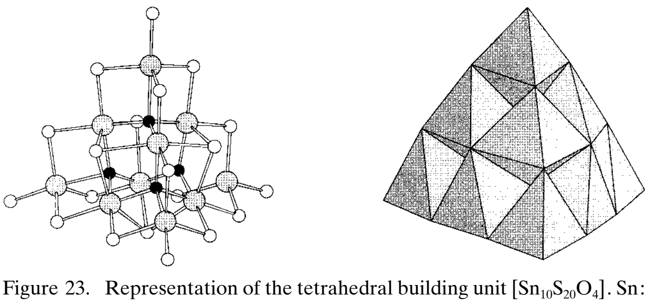

Figure 23. Representation of the tetrahedral building unit $[Sn_{10}S_{20}O_4]$. Sn: large grey spheres, S: small white spheres, O: small black spheres.

atoms to give rise to a distorted trigonal bipyramid. Each oxygen atom is linked to four tin atoms whereas the sulfur atoms connect two or three tin atoms together. The arrangement of the super tetrahedra blocks is related to that of the [SiO_4] units in the cristobalite-type structure. A lamellar phase built up from similar decameric units was also isolated.[210]

The structures of the germanium and tin sulfides consist of a few well-defined building units that are for the most part based on tetrahedral geometries, as in the zeolites and many phosphate derivatives. The synthesis of antimony sulfides has yielded completely different geometries, probably due to the influence of the lone pair of electrons of antimony(III). Several different situations are observed. In the phase synthesized with tetramethylammonium, (Me_4N)[Sb_2S_5],[214] the antimony atom is surrounded by four sulfur atoms with a pseudo-trigonal-bipyramidal configuration; the lone pair forms the fifth vertex and is located in the trigonal plane of this polyhedron. The three-dimensional network is entirely built up from edge-shared bipyramids, ψ-[SbS_4] (ψ corresponds to a missing ligand as a result of the lone pair of antimony). However, in other compounds,[215, 216] the coordination of antimony may vary from 3 to 5 and the corresponding polyhedra may be ψ-[SbS_3] tetrahedra, or ψ_2-[SbS_4] and ψ-[SbS_5] octahedra. In general, these polyhedra share edges and corners to form infinite ribbons, and the interconnection of the ribbons generates open frameworks with different systems of channels in which the organic molecules are located. As observed in the tin phosphates (see Section 5.3), the lone pairs point towards the centers of the channels. Similar structural features have been reported in lamellar antimony sulfides.[217]

Very recently, one example of an indium sulfide has been described by Parise and co-workers.[198] The open framework is based on corner-linked supertetrahedral [$In_{10}S_{20}$]$^{10-}$ clusters. The same building-block configuration was obtained with the tin oxysulfide,[213] but the indium atom is tetrahedrally coordinated by sulfur. The connection of these tetrahedral units is related to two interpenetrating, nonintersecting diamondlike lattices.

Little is known about the properties and potential applications of the open-framework chalcogenides, though Jiang and co-workers[218] have recently described the adsorption and spectroscopic properties of some of the layered tin sulfides that belong to this family of materials. Furthermore, the very recently discovered indium sulfides, ASU-31 and ASU-32, which are large-pore systems based upon linked supertetrahedra containing 10 [InS_4] units, exhibit interesting ion-exchange properties.[219]

6.2. Halides

In 1997, Martin and Greenwood[220] introduced a new generation of microporous compounds which utilized halides as replacements for the normal oxygen or chalcogenide anions. New materials were formed from metal halides such as zinc dichloride and copper chloride; Zn and Cu are both known to exhibit tetrahedral geometries with chlorine. Three compounds, named CZX-*n*, have been synthesized under hydrothermal conditions (160 °C) in benzene solution. The framework of CZX-1 is isostructural with the aluminosilicate sodalite (SOD), while CZX-2 and CZX-3 adopt new framework topologies. All three structures are based on $ZnCl_4$ and $CuCl_4$ tetrahedra sharing corners, as in the aluminosilicate zeolites, and the organic molecules are trapped in the micropores. One interesting property of these microporous halides is their high capacity to adsorb methanol into the framework. They can adsorb up to three equivalents per framework unit, but the addition of more methanol results in dissolution of the structure and the formation of a colloidal solution.

6.3. Nitrides

The existence of condensed framework structures based upon ceramic nitrides, such as the silicon nitrides of composition Si_3N_4, led to the idea that the synthesis of open-framework nitrides might also be feasible. The first success in this area was the preparation of the phosphorus nitride, $Zn_7[P_{12}N_{24}]Cl_2$, by Schnick in 1992.[221a] This was achieved by means of a high-temperature (700–800 °C) solid-state reaction between $ZnCl_2$ and HPN_2, and yielded a small-pore open framework with the sodalite structure. A similar reaction, in which a source of oxygen ($OP(NH_2)_3$) was also included in the reaction mixture, has very recently led to the discovery of a phosphorus oxonitride with the same structure.[221b] The preparation of open-framework silicon nitrides requires more severe conditions, but Schnick successfully achieved this objective in 1997 with the synthesis of the small-pore zeolitic $Ba_2Nd_7Si_{11}N_{23}$.[222] In this instance, reaction between the metals and silicon diimide, $Si(NH)_2$, under a nitrogen atmosphere in an RF furnace operating at temperatures between 900 and 1650 °C, was necessary. By analogy with the progress in other areas, it seems probable that much milder reaction conditions will be necessary if the preparation of large-pore nitrides is to be achieved.

7. Binary Metal Oxides

Whereas the development of crystalline, open frameworks based upon silicates, phosphates, and related materials has progressed at an ever-increasing pace, the synthesis of simple binary oxides with periodic open structures has been less successful to date. An obvious exception to this generalization, however, is the case of MnO_2, which is known to exhibit small channels up to about 7 Å in diameter in the minerals hollandite, cryptomelane, and todorokite. Synthetic analogues of these minerals have been made[189, 223] in the presence of metallic cations (M) such as Mn^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}. They are based upon a structural principle in which octahedral [MnO_6] units share edges and the metallic cations occupy the channels, and correspond to a stoichiometry of $M_xMnO_2 \cdot nH_2O$ in the as-synthesized form. As a consequence, these are mixed-valence materials with a manganese oxidation state typically in the range 3.5–3.8, and they show a variety of interesting electronic, magnetic, and catalytic properties.[224, 225] A small concentration of manganese vacancies is often observed, and a limited amount of manganese substitution is also possible. The water of hydration can be removed at temperatures up to about 500 °C, to yield nanoporous materials that will adsorb small organic molecules such as cyclohexane.

The existence of these stable open frameworks in the specific case of manganese is presumably related to the high ligand field stabilization energy associated with the t_{2g}^3 electronic configuration of Mn^{4+}. This should render the materials kinetically stable with respect to their collapse into more condensed phases. It is also, no doubt, the reason why it has been possible to make stable mesoporous phases based upon MnO_2, and indeed to remove the surfactant templates in order to access their porosity.[226]

8. Open-Framework Coordination Compounds

In a domain where the challenge is often to increase and modulate the sizes of the pores for selective adsorption and other applications, purely inorganic systems have their limitations owing to the relatively small sizes of the polyhedral centers and their limited means of connection. As an alternative strategy for achieving this end, it is possible again to use organic molecules, but this time in the skeleton rather than within the pores. This has led to a new chemistry that we can consider to be “non templated”, since the holes are not occupied by the usual templates of the zeolite-related chemistry. Some aspects of this area have recently been reviewed.[227]

Two approaches have been developed since the beginning of the 1990s. The first concerns the modification of previously known porous solids by replacement of the phosphate groups with other chelating agents in the structure, mainly organic phosphonates and carboxylates. Most of these organic linkages are reasonably flexible. This will be discussed in the first section. The second starts from rigid organic moieties, with a preselected shape, which are then connected, either by strong ionocovalent bonds with metallic centers or by appropriate hydrogen bonding.

8.1. Organically Modified Inorganic Open Frameworks

The initial idea in this area was to replace phosphates by phosphonates to produce open frameworks. This strategy was originally used for layered compounds by Alberti[228] in order to increase the interlayer spacing in such materials. The approach took advantage of monophosphonates, which acted as spacers between the layers, with no possibility of connection between them.

In the context of building open three-dimensional frameworks, it is possible to create connections between layers by the use of diphosphonates or functionalized monophosphonates. This idea, initiated by Johnson and Jacobson,[229] is currently used by several groups (e.g. Zubieta in USA,[230] Bujoli[231] and Férey[232, 233] in France) and leads to three-dimensional transition metal phosphonates with various topologies,[234] the two most spectacular examples being $[M(O_3PCH_2NH(C_2H_4)_2NHCH_2PO_3)]\cdot H_2O$ (M = Mn,Co) and $[NH_4]_4[(V^{IV}O)_3(O_3PCH_2PO_3)_4(H_2O)_4]\cdot 4H_2O$. The first[230] is made from tetrameric $[Co_2P_2]$ entities linked by $CH_2NH(C_2H_4)_2NHCH_2$ groups in three directions. The long connections between the tetramers lead to very large, ellipsoidal 44-rings (4.7 × 18 Å) which contain water molecules. The second,[232] using vanadium, leads to clover-like windows (Figure 24) in which ammonium ions and water molecules lie. Such an approach, successful with the 3d transition metals, is also valuable for lanthanides.[233] A whole series of lanthanide phosphonates has recently been characterized, thus underlining the generality of the method.

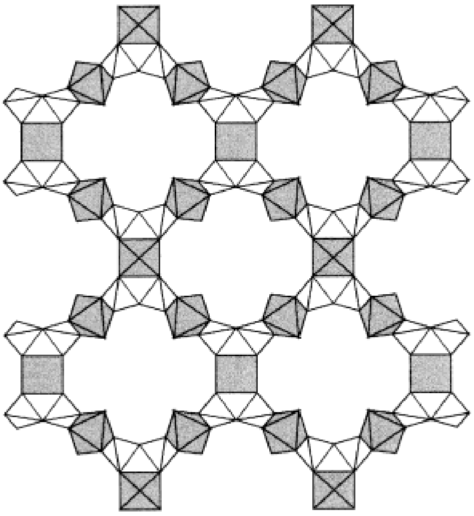

Figure 24. Projection of the structure of $(VO)_2VO(H_2O)_4\{O_3P\text{-}CH_2\text{-}PO_3\}_4$, MIL-2.

However, the use of diphosphonates turns out not to be essential in order to make an open framework, since a few examples show that this can even be achieved with monophosphonates. Thus, three-dimensional zeolite-like phosphonates have been reported for β-$Cu(O_3PCH_3)$,[235] $Zn(O_3PC_2H_4NH_2)$,[236] and β-$Al_2(CH_3PO_3)_3\cdot H_2O$,[90] the latter having unidimensional 18-ring channels with a 5.8 Å cross-section (see Section 3.6).

A new variant of this approach, which uses carboxylates instead of phosphonates, has led to new lanthanide(III) glutarates and Co^{II} succinates with open frameworks.[237] In the first, parallel chains of edge-sharing polyhedra of Ln are connected in the other two directions by glutarate bridges, thus generating voids that can be occupied by water; the water can be removed and readsorbed, reversibly, on heating and cooling.[237c] In the second, layers of edge-sharing Co^{II} octahedra with 12-ring windows are pillared by succinate chains.

The carboxylate approach has very recently been extended by utilizing benzene-1,3,5-tricarboxylate (TMA) to link dimeric copper units to form a highly porous metal coordination polymer known as HKUST-1.[238] The framework is stable up to 240 °C and exhibits promising adsorption properties. It is believed that the pores can be chemically functionalized by replacement of the aqua ligands that are attached to the copper ions. Since the TMA is a fairly rigid organic link, HKUST-1 could also be considered in the context of the following Section 8.2.

The simplest members of the dicarboxylate class of materials are the oxalates, which are also capable of forming open frameworks, both with rare-earth elements[239] and with tin(II).[240] The latter example is particularly interesting, since it involved the use of an organic template, guanidinium, for the first time in this area. In another variation on the carboxylate theme, an open-framework Co^{II} system containing a mixed carboxylate–phosphonate ligand has also been reported recently.[241]

8.2. Open Frameworks with Rigid Organic Links

The development of this area can be traced back to the work of Gravereau, Garnier, and Hardy in Poitiers in the late 1970s, in which zeolitic materials exhibiting ion-exchange properties were made by the linkage of hexacyanoferrates units with (tetrahedrally coordinated) Zn^{2+} cations.[242] Charge balance is provided by sodium ions. The concept gained fresh impetus in 1994 with the work of Robson[243] and J. Moore.[244] In a general way, and even if their approaches were different, their aim was to recreate the topologies of zeolites and related open frameworks in organic and metal–organic solids in order to create large and adjustable cavities. The latter might be used for therapeutic applications, such as the selection, in a single step, of the active form of a drug.

Compared to inorganic open frameworks in which strong semi-ionic bonds govern the structure, this approach has the advantage of harnessing a diversity of bonding types (semi-ionic, covalent, and hydrogen bonding) to modulate the topology. Starting from this idea—the use of pre-selected organic moieties—one can, however, distinguish two main classes of compounds based on the linking modes between them. The linkage can occur either over strong bonds (often M–N bonds) of metallic centers of appropriate coordination, or by weak hydrogen bonds. In both cases, the stability is typically less than that found in most inorganic open frameworks.

Robson[243] choose as a geometrical/topological model one of a number of simple three-dimensional nets such as diamond, α-Po, and PtS, and then tried to devise ways of chemically linking together the building blocks with a functionality and a stereochemistry appropriate to the chosen parent net. Using this approach, he linked metalloporphyrines like $[Cu^{II}(tcp)]$ or $[Cu^{II}(tpp)]$ by means of Cu^{I} complexes to generate open frameworks of ca. 24×20 Å diameter, the tunnels being occupied by disordered molecules of solvent (tcp = 5,10,15,20-tetrachloro porphinate, tpp = 5,10,15,20-tetraphenyl porphinate). The first success of Lee and Moore[244] concerned $[Ag(TCB)(CF_3SO_3)]$ (TCB = 1,3,5-tricyanobenzene). TCB has threefold symmetry and its terminal nitrogen atoms serve as ligating groups for the soft Ag^{I} cation. The combination of TCB and Ag^{I} triflate leads to a honeycomb lattice in which tricoordinated Ag links three TCB units with dimensions of ca. 10 Å to form cavities, in the centers of which are the triflate anions. The layers are stacked in an ABCABC manner. An extension of the concept with more complicated molecules has been described.[245]

A similar methodology has been developed simultaneously by Yaghi.[246] In this instance, he used 4,4′-bipyridine as the organic component, using the two nitrogen atoms of the molecule for ligation. This led to three-dimensional compounds with interpenetrating subnetworks; the cations used were Cu_2Cl_2 dimers, Cu and Ag.[247] The same principle was applied to Zn associated with SiF_6.[248] It is noteworthy that the cavities generated in this family of compounds accommodate either solvent molecules or, more often, anions, at variance to the situation in zeolites.

The second approach used hydrogen bonding between organic moieties. The most beautiful example was provided by Wuest et al.[249] who used a tetrahedral tecton with Si surrounded by four pyridone rings, to produce a framework built up from hydrogen bonding between these tectons. The same principle was applied by Moore[244] to synthesize an organic solid with wide channels based on hydrogen bonding between macrocycles composed of six phenol groups linked by six acetylenic bonds. Solvent molecules occupy the centers of the macrocycles.

9. Future Developments

Whatever future discoveries may lie ahead, we can look back and see that there was clearly a watershed with the synthesis of open-framework aluminum phosphates by Flanigen and colleagues in 1982.[23] The impact was not felt immediately, except in the context of $AlPO_4$s and $GaPO_4$s, but this discovery gradually led to the realization that the aluminosilicate zeolites might only be the tip of the iceberg in the field of nanoporous crystalline materials. The growing chemical and structural diversity of open-framework materials is amply illustrated by the many examples cited in the preceding sections. In terms of phosphate-based materials, for example, the list is already very impressive, with at least as many as fourteen elements now known to form open-framework structures. This pattern of behavior is underpinned by the strength of the P–O bond, which is broadly comparable with those of Si–O and Al–O, so the relative stabilities within this family of M-P-O materials are probably determined by the M–O bond strengths. As the size and coordination number of M increases, the M–O bond energy decreases, so it is not surprising that the $AlPO_4$s, especially those that contain tetrahedral Al, show good stability compared with say, $GaPO_4$s and $InPO_4$s. However, some interesting materials have yet to be synthesized. For example, $Cr^{III}PO_4$s would surely show excellent kinetic and thermodynamic stability, given the large ligand field stabilization energy of octahedrally coordinated Cr^{III}, and similar predictions could be made with respect to some of the heavier transition metals, such as Pt^{II} or Rh^{III}. The same argument could be applied to other compounds of these stable transition metal ions, such as their binary oxides, as is already apparent in the case of open frameworks based upon MnO_2 (Section 7).

The recent discovery of new materials based upon transition metal ions inspires us to contemplate the possibility of making open frameworks that exhibit some of the remarkable electronic properties of condensed transition metal compounds. What sort of exciting applications, for example, might be possible with nanoporous crystalline materials that exhibit ferromagnetism, metal-semiconductor transitions, giant magnetoresistance, ferroelectricity, combined ionic/electrical conductivity, or even superconductivity? Some of these developments will surely be seen in the not-too-distant future. Similarly, whilst the overwhelming majority of the known oxide-containing open frameworks are transparent insulators, we are beginning to see narrow band gap materials, and perhaps even metals, in the case of the chalcogenides (Section 6.1). We can also be encouraged by the news that open frameworks containing rare-earth ions are also possible (Section 8.1), and here we could speculate about the possible existence of nanoporous optical and magnetic materials, such as open-framework analogues of the Nd-YAG (yttrium aluminum garnet) lasers and YIG (yttrium iron garnet) permanent magnets. Even the possibility of nanoporous actinide compounds now seems within reach in view of the recent discovery of an open-framework uranium oxyfluoride.[250]

The scope of this field is not limited by nature itself, since the number of hypothetical, three-dimensional framework topologies is infinite,[251] but it is limited by the creativity of the synthetic chemist. New preparative strategies continue to appear, such as the use of different solvent systems,[49, 50] the synthesis of new organic template molecules,[252] and the construction of open frameworks from molecular building blocks (Section 8). The use of computational methods in the design of organic templates for the synthesis of novel architectures is also of great interest.[253] And at the opposite end of the spectrum, automated combinatorial methods, which have been successfully applied in other areas,[254] are now being applied to the synthesis of open frameworks, which would allow as many as 1000 samples to be prepared in a single experiment.[255]

In conclusion, it is clear that a vast field of new and exciting materials is rapidly emerging from the world of aluminosilicate zeolites. In the industrial environment, the emphasis for the time-being will continue to be on the use of aluminosilicates for ion exchange, separation, and catalysis, but we can look forward to a future in which the materials and their applications will be far more diverse.[256] Indeed, in dedicating this review to the memory of our friend, Jean Rouxel, it is not unreasonable to expect that the rich tapestry of transition metal chalcogenides that he discovered and elucidated will soon find their parallel in the realm of open-framework materials.

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