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Nanoporous Structures by Design

Michael J. Zaworotko*

Whereas the development of reliable methods for crystal-structure prediction remains an elusive scientific challenge,[1] its relevance to aspects of pharmaceutical and materials science has fueled rapid development of the concept of crystal engineering.[2] Is crystal engineering synonymous with crystal-structure prediction? The simplest answer is, not yet. However, crystal engineering has emerged as a paradigm for the design and synthesis of new solid phases because its fundamental precept is that most crystal structures can be regarded as self-assembled entities,[3] that is, they are "supermolecules par excellence".[4] In other words, crystal engineering can be regarded as being synonymous with supramolecular synthesis.

Crystal engineering has thus far focused upon chemical entities that are predisposed to form predictable, self-assembled networks that is, molecules or ions that are exofunctional and capable of forming 1D, 2D, or 3D networks. Crystal structure prediction is therefore simplified to an issue more related to the design of networks. That such a strategy can be successful is perhaps best exemplified by the recent observation of several new classes of open framework solids that exhibit the property of microporosity.

Zeolites represent the prototypal microporous solids, have channels and cavities of 4–10 Å,[5] and have found widespread application in catalysis and separations.[6] The first generation of synthetic "zeolite analogues" that were generated by crystal-engineering strategies consisted of rigid 3D networks based upon organic or metal–organic moieties. However, these zeolite analogues typically suffered from the phenomenon of interpenetration[7] or from the irreversible collapse of the structure upon the removal of the guest molecules. Subsequent studies revealed a second generation of frameworks that are more closely analogous to zeolites in that they are robust enough to survive the complete loss of the guest molecules and that they reversibly adsorb small volatile molecules. Interestingly, such structures can be purely organic and sustained by hydrogen bonds[8] or they can be based upon coordination-polymer frameworks.[9] However, these compounds do not compare to the inorganic (zeolite) structures in terms of either their surface area or their thermal stability.

Very recently, a third generation of synthetic frameworks that exhibit hitherto unseen levels of porosity, so called nanoporosity, and stability has been discovered. These structures are exemplified by the octahedral polymer $[Zn_4O(bdc)_3]$ (bdc = benzene-1,4-dicarboxylate).[10] $[Zn_4O(bdc)_3]$ is a relatively simple and inexpensive material to prepare, is remarkably stable to loss or exchange of guests, and remains crystalline at temperatures above 300 °C. The feature that makes $[Zn_4O(bdc)_3]$ special is that it exhibits a relative degree of porosity hitherto unprecedented in crystalline solids. Recently Kitagawa and co-workers reported the structure and porous nature of $[Cu(4,4'\text{-bipy})_2](SiF_6)$ (**1**)[11] (bipy = bipyridine). Complex **1** is the latest addition to this new family of nanoporous materials and is important because of its implications for future design principles and because of its properties.

Design Principles

It would be natural to assume that 3D architectures present a higher level of complexity than 1D and 2D architectures. In many ways 3D architectures represent the ultimate challenge to crystal engineers since success leads directly to the control and prediction of crystal structures. It is therefore somewhat ironic that two of the simplest examples of predictable networks are exemplified by 3D networks, that is, those generated by the assembly of tetrahedral or octahedral nodes. Tetrahedral nodes are predisposed to generate diamondoid architectures, whereas octahedral nodes are expected to afford octahedral networks.

Diamondoid architectures using a tetrahedral metal as the node and cyanide ligands (CN^-) as the spacer represent

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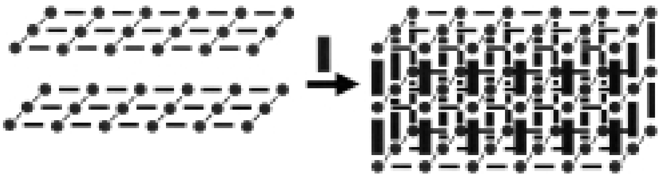
prototypal examples of diamondoid coordination polymers. The compounds $Zn(CN)_2$ and $Cd(CN)_2$ form diamondoid networks with twofold interpenetration.[12] However, $Cd(CN)_2$ can also be obtained as a single network in which CCl_4 fills the cavity.[12c] This result illustrates two principles that have broad implications: 1) interpenetration can be avoided in the presence of an appropriate template or guest molecule, and 2) such compounds might be regarded as catenated and noncatenated supramolecular isomers[13] of each other.

Octahedral coordination polymers are exemplified by Prussian Blue, which is in a sense an octahedral version of $Cd(CN)_2$. Prussian Blue avoids interpenetration because the cavities in the framework are filled by counterions. Synthetic octahedral networks were first reported in 1995. The complex $[Ag(pyrazine)_3]SbF_6$[14] is sustained by octahedral Ag^I cations and pyrazine ligands that are relatively short compared to other bridging ligands; the framework is necessarily cationic. The zinc analogue of **1** $[Zn(4,4'\text{-bipy})_2](SiF_6)$ is a neutral framework and isostructural with **1**.[15] Both these compounds represent a slightly different approach to building 3D structures, that is, the manipulation of existing 2D structures by cross-linking. Such a strategy is feasible if one selects an appropriate 2D structure that has functional groups aligned in the vertical direction and that resembles the "pillaring" effect in clays. Compound **1** can be regarded as having been generated from square grid coordination polymers[16] that are cross-linked by μ-SiF_6 anions. The SiF_6^{2-} counterions cross-link the square grids made by Zn centers and 4,4′-bipy ligands to form a rigid pseudooctahedral polymer with very predictable shape and dimensions (Scheme 1). Furthermore, the wall-like 4,4′-bipy ligands make it impossible for the structure to interpenetrate. Perhaps the most salient feature of **1** from a design perspective is that not only is the structure rational, it is entirely predictable. Indeed, **1** crystallizes in space group $P4/mmm$ with $Z=1$. In other words, the point group at the Zn and Cu centers (D_{4h}) is propagated into the space group symmetry. Furthermore, the cell parameters are effectively predetermined by the intermetallic separations.



Scheme 1. From square grids to octahedral polymers. ● octahedral moiety (i.e. metal), ▬ linear bifunctional ligand alternate linear ligand (e.g. anion).

Properties

The channels in **1** have an effective cross-section of approximately 8 × 8 Å and represent almost 50% of the volume of the crystal. Solvent molecules are readily eliminated and, remarkably, the structure remains intact at 373 K under vacuum. The pseudooctahedral framework has a large surface area that remains accessible to guest molecules (Figure 1). Indeed, the surface area of **1** is such that its capacity for methane gas adsorption is significantly greater, almost double, that of zeolite 5A, which had previously been the solid with the highest measured methane adsorption capacity.[11] Indeed, **1** and $[Zn_4O(bdc)_3]$ (approximately 60% of the structure is available and accessible in $[Zn_4O(bdc)_3]$) offer significant increases over the typical accessibility of about 30% seen in zeolites.[5]

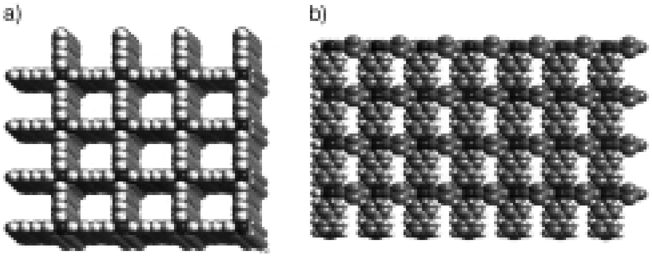


Figure 1. $[\{Cu(4,4'\text{-bipy})_2\}_n](SiF_6)_n$—an octahedral coordination polymer with large channels. a) *ab* plane. b) *ac*/*bc* planes

The Future

The ability to design networks from first principles affords a method to control and fine tune the shape and molecular recognition features of porous structures. Even for pseudooctahedral networks the diversity of components that are readily available and the means by which they can assemble spans the full range of chemistry. A work of M. C. Escher (Figure 2) offers a perspective that perfectly illustrates the situation—in principle, any octahedral moiety (for example a metal or a metal cluster) can serve as a node and the "spacer" can be a wide range of readily available ligands. It therefore seems

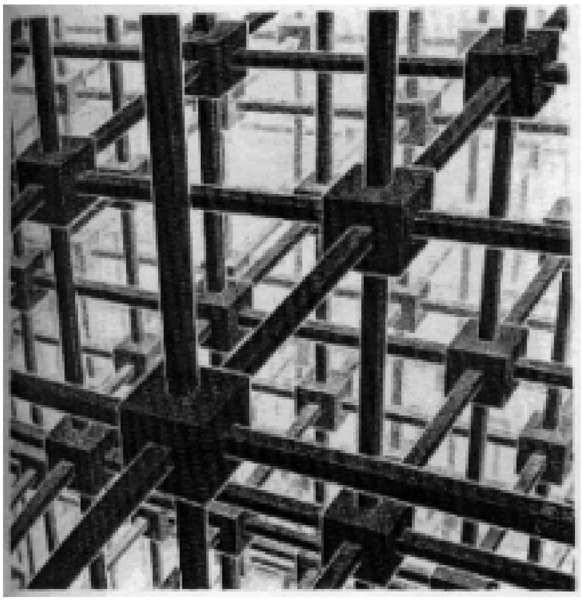


Figure 2. M. C. Escher's "Cubic Space Filling" reprinted with permission from Cordon Art B.V. copyright © Baarm, Holland 2000. All rights reserved.

plausible to assert that we have thus far only observed the prototypes of what should become a wide range of synthetic, designed coordination polymers. Furthermore, nanoporosity represents just one possible property of such solids. As the size of channels and cavities increases, the possibility of porous structures that can hold medium to large organic compounds and biomolecules becomes evident. We could therefore see applications in the areas of green chemistry (for example nanoscale reaction flasks for catalysis) and materials science (biocomposite materials for sensors, polar inclusion compounds). And what about crystal structure prediction? It remains a challenge of the highest order and has great relevance in its own right. However, it is not a prerequisite for the design of new structures. In the words of von Schnering, "The peasant who wants to harvest in his lifetime cannot wait for the ab initio theory of weather".[17]

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