

PREFACE

Design of Solids from Molecular Building Blocks: Golden Opportunities for Solid State Chemistry

Solid state chemists have long dreamed of the day when they could synthesize materials that were designed *a priori* to have structures that would lead to specified functions. This still remains an elusive goal in solid state chemistry, although it is almost commonplace in molecular chemistry; indeed a major part of the pharmaceutical industry involves the synthesis of molecules previously designed to have a specific physiological action. In metal-complex chemistry, organometallic compounds are routinely designed to exhibit well-defined catalytic action, and complex clusters are assembled and studied as functional models of metalloenzymes. On the other hand, it is rare indeed that synthesis of new extended (i.e., nonmolecular) materials really proceeds from prior design of a specific desired structure; what usually happens is that an experiment is intelligently planned so that it will yield materials with structures that are possibly of interest. This is mainly because molecules can be manipulated one step at a time whereas most solids typically are assembled in a single step. Thus, step-by-step control is lost and success of the final outcome depends on cleverly and carefully selected starting materials and reaction conditions. Nevertheless, considerable progress has been made by employing distinct molecular entities as building blocks in the solution assembly of solids, and this Special Issue of the *Journal of Solid State Chemistry* is devoted to assessing the state of the art and erecting some signposts to promising future directions.

From the very early days of crystal chemistry it was recognized that the structures of complex crystals could fruitfully be described in terms of units variously called modules, building units, structural units, or secondary building units. Many of the early structures determined were those of minerals, and modular description plays an important role in systematic mineralogy. In many instances structural description is greatly simplified by a description in which individual atoms of simple structures (e.g., those of NaCl, ZnS, CaF₂) are replaced by clusters of atoms. It is important to note, however, that the description is an *a posteriori* one.

More recently it has been realized that the assembly of building blocks yields extended structures with designed

properties. An important and new aspect is that the structure appears *a priori* as a target of synthesis. It is with this aspect of the subject—the *design* of extended solids from modules—that this Special Issue is concerned. Considerable attention is usually given to factors such as solvent composition, catalytic action, cluster formation in solution, and interaction with solvent or other molecules that may serve as guests, indeed to most of the formidable arsenal of techniques developed over the years by molecular chemists. This is in sharp contrast to the “shake and bake” and “heat and beat” methods so characteristic (and fruitful in skilled hands!) of the early days of solid state chemistry. Indeed one of the most rapidly growing and productive areas of solid state chemistry is the design of organic and particularly metal–organic extended solids, and it is no coincidence that they figure prominently here.

The range and diversity of structures and compositions that can be produced by the building block approach have motivated our presentation of a tutorial article at the beginning of the issue. Its aim is to provide a description of the most simple and most likely nets to be adopted by assembled solids. Special emphasis is based on low-density (“open framework”), porous solids constructed by combining molecular (i.e., polyatomic) clusters that have well-defined linking sites with linking groups that may be linear or branched. Although such solids have been referred to interchangeably as “porous” and “open,” it is our preference to categorize these solids according to mobility of species occupying their cavities. The usage of the term “open framework” to refer to any low-density or large-scale structure is not entirely appropriate since “open” implies allowing passage, as in “open” door or window. In many cases that property is absent (or at least undetermined in the structure in question) because passage is hindered by solvent molecules or counterions which form strong interactions with the framework; as a result, they are necessary to maintaining the integrity of the crystal structure. Such compounds, although nonporous, may be valuable in other applications (optics or magnets) where porosity is not required. However, in cases where sorption and desorption are hindered, we find it informative and perhaps appropriate to refer to such

structures as *cacoxenates*.¹ But we do insist that “porous” implies having pores, and a pore is, in the OED definition, a “minute ... opening ... through which fluids or gases can pass.” *Clathrates*, in which molecules are trapped, are not porous, although in the usage referred to (and reluctantly accepted) above, they may be open. We note in passing that the passage of water or atoms is rather common, and in the present context we would not include materials such as beryl, which readily takes up helium, as “porous.” Porous materials are classified by IUPAC based on their pore diameter, d : microporous for $d < 20 \text{ \AA}$, mesoporous for $20 \text{ \AA} \leq d \leq 500 \text{ \AA}$, and macroporous for $d > 500 \text{ \AA}$. Recently there has been reference to nanoporous materials for structures having pores of 10–100 \AA diameters.

Zeolites are microporous aluminosilicates; purists will insist that they are naturally occurring (minerals), but the term has come to be widely used to include other synthetic oxides (e.g., aluminophosphates). One even hears of “organic zeolites” but this is used mainly for organic clathrates, and very few all-organic porous materials have yet been achieved. At the very least, terms such as “zeolite-like” should be restricted to materials in which sorption–desorption and/or exchange have been *demonstrated*.

The great potential for application of the building block approach to the construction of inorganic solids with useful properties remains largely untapped, although recent progress indicates some possibilities. For example, the design of metal organic networks with polar building blocks and mixed valence metal ions has provided materials with non-linear optical and magnetic properties. The use of porphyrins and metallocrown-based solids as building blocks has yielded materials with potential for chiral separation and recognition. Metal centers such as Ti(IV) have been employed in the construction of covalent aryloxide frameworks for their potential as solid catalysts with specific properties.

In this Special Issue, several contributors provide elegant examples of the use of inorganic clusters as building blocks to yield giant molecules and sulfide-based mesoporous materials. Although less emphasized here, the construction of large molecules and extended structures using weak forces such as hydrogen bonds is another attractive strategy for

designing intricate shapes that potentially could be used in the transport and selective encapsulation of organic molecules from dilute solutions.

The reader can see some of the steps being taken by chemists as they attempt to increase the rationality of their synthetic work by employing both innovative building block approaches and gentler synthetic techniques which allow the use of such molecular chemistry concepts as kinetic control and polyatomic building blocks. Solid state and molecular chemists have become very interested in the designed aggregation of discrete fragments into larger and larger assemblies. We are all now well aware of the value of understanding structure as a necessary prerequisite to synthesizing materials with specific bulk properties. Hence, the traditional “molecular” and “solid state” boundaries are coming down in order to reach the same goal: exploitation of structure/property relationships. Undoubtedly, solid state chemistry is a fertile ground for those with creative, broad-ranging approaches.

The process of transforming molecular complexes and clusters to extended solids, as illustrated in this issue, is essential not only to translating molecular geometry into assembled structures but also to converting molecular reactivity into desired physical properties. Recognition and implementation of this strategy make the design of bespoke functional solids a realizable goal. In this context it is worth recalling that the complex and beautiful structures that are being reported with increasing frequency could not have been routinely produced just one or two decades ago. New developments in structure elucidation, especially by crystallography (CCD cameras for data collection, direct methods, etc.) and by NMR (solid state, multidimensional, etc.), have truly led to a renaissance in solid state chemistry and related areas such as supramolecular chemistry. We are fortunate to participate in what we believe is developing into a golden age.

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¹From the Greek *Kakos*, “bad,” and *xenos*, “guest or stranger” (the consummate bad behavior of a guest is refusing to leave without destroying the house). Ironically, the mineral cacoxenite [P. B. Moore and J. Shen, *Nature* **306**, 356–358 (1983)] is very often cited as an exemplar of an open structure. However, although the structure contains large channels, these are filled with water, and the structure collapses if the water is removed. In this context we recall the exchange from Shakespeare’s *Macbeth*: “Doctor: You see, her eyes are open. Gentlewoman: Ay, but their sense is shut.”