Figure 18. Illustration of the crystal packing of the hydrogen-bonded 2D networks in $[(BTC^{2-})(NH_2(CH_2Ph)_2^+)_2]$. The benzyl moieties preclude interdigitation and facilitate reversible sorption of aromatic molecules.

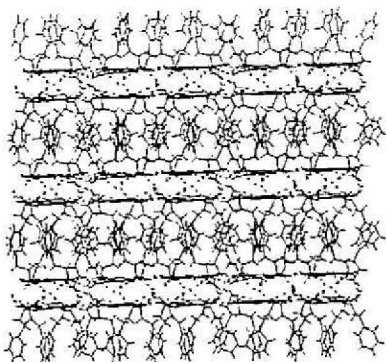**Figure 19.** Illustration of the crystal packing in $[(BTC^{2-})-(NH_3(CH_2Ph)^+)_2]$, a prototypal example of the network structures formed by BTC dianions and primary ammonium cations.

Figure 20. Modular honeycomb network sustained by BTC trianions and secondary alkylammonium cations: (a) schematic representation of the hydrogen-bonding pattern and (b) space-filling illustration of the crystal structure of $[(BTC^{2-})(NH_3(C_6H_{12})^+)_2]$.

structure is illustrated in Figure 18, and as should be clear, there is no interdigitation of benzyl groups. The guest molecules interact with walls of the channels only, and the asymmetric unit is unusual: 3:3:1 for host:guest:solvent. In the presence of primary ammonium cations, similar structures are obtained but they are more appropriately termed bilayer architectures since there are alternating hydrophobic and hydrophilic regions. A typical structure is illustrated in Figure 19. Similar structures are obtained for both alkyl- and benzylammonium cations. It might be reasonable to describe such structures as being cytomimetic since there is a resemblance to the type of supramolecular synthons that exist in phospholipid membranes and in the solid phases of surfactants. The ancillary organic groups orient in the same direction and interdigitate with adjacent layers to generate hydrophobic regions. The hydrophilic faces of adjacent bilayers also face one another and can incorporate water molecules. The thickness of hydrophilic layers ranges from 3.2 to 3.4 Å, while the thickness of interdigitated layers increases with the size of the organic group.

Stoichiometry 1:3 (H₃TMA:amine). In principle, 1:3 stoichiometry offers the opportunity to generate honeycomb networks. As revealed by Figure 20a, motif A or B should be capable of propagating the trimesate anion into a honeycomb structure. Figure 20b reveals that the crystal structure of [TMA]-[dicylohexylammonium]₃ exists as the anticipated honeycomb array.[290] The cyclohexyl moieties, which are omitted for the sake of clarity, effectively prevent interpenetration by capping the 13 Å cavities that are present within the honeycomb structure. If the
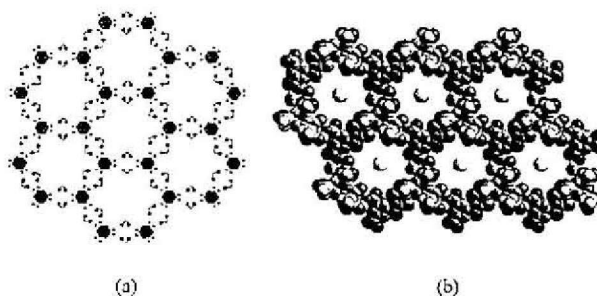
solvent is changed, a honeycomb network based upon the other supramolecular synthon is generated,[293] and it has been reported that this form of the honeycomb network will self-assemble at the air—water interface. The modular nature of this structure permits replacement of the cyclohexyl moieties by other moieties. In this context, alkyl groups that are less sterically demanding (e.g., n-alkyl) have also been incorporated into the motif in Figure 20a. Interpenetration occurs in these structures.

Guanidinium Sulfonates. A series of related structures that are based upon two-dimensional layers resulting from hydrogen bonding of the trigonal guanidinium cation, $C(NH_2)_3^+$, and organic sulfonate ions RSO_3^- has been extensively studied by the Ward group[176,238,240,295–302] (Scheme 14).

Interdigitation of the organic substituent of the sulfonate ions on adjacent layers and ionic hydrogen-bonding predictably leads to a broad series of laminar architectures. It should be noted that there are several key differences between guanidinium sulfonates and alkylammonium trimesates. (1) There exists only one ancillary organic functional group per sulfonate ion compared to up to two ancillary functional groups per ammonium cation. (2) The anion is functionalized rather than the cation. (3) In one sense, the alkylsulfonates are more versatile since they can exhibit architectural (i.e., supramolecular) isomerism so as to generate either bilayer or clay-like architectures. To generate a clay-like architecture, organic groups must orient above and below each layer as illustrated by Scheme 15. The steric demands of the organic group appear to determine whether they orient in the same direction (i.e., a bilayer structure) or alternate above and below the layer (i.e., a clay-like structure).

C. 3D Networks

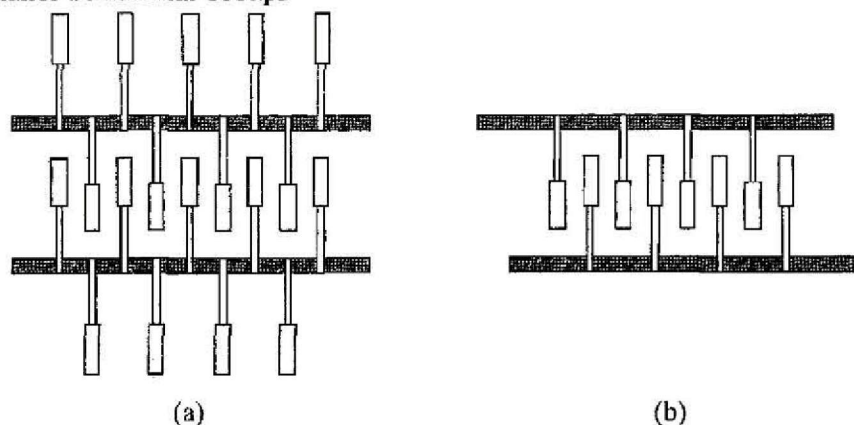### 1. Self-Assembled Hydrogen-Bonded Diamondoid Networks

A report by Ermer[86] on the structural characterization of adamantane-1,3,5,7-tetracarboxylic acid and its implications represented a watershed for crystal engineering. Ermer's study was followed by a flurry of activity into design from first principles of both organic diamondoid networks and metal—organic diamondoid coordination polymers. The carboxylic

Scheme 14. Schematic Illustration of the Key Structural Features of Guanidinium Sulfonates: (a) Hexagonal Channels that Form 2D Honeycomb Networks and (b) Two Extended Structures (2D and 3D) that Can Result from the Self-assembly of Guanidinium Cations with Disulfonates Anions

(a)   (b)
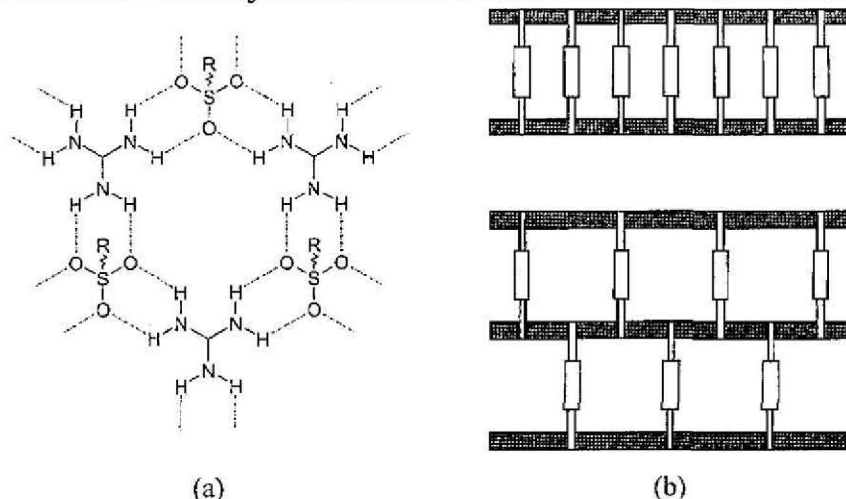
Scheme 15. Schematic Illustrating Two Possible Modes of Interdigitation for Guanidinium Sulfonates: (a) Clay-like, Induced by Sterically Demanding Functional Groups and (b) Bilayer Architecture, Typically Observed for Smaller Functional Groups

(a)   (b)

acid groups of adamantane-1,3,5,7-tetracarboxylic acid are tetrahedrally oriented. It is therefore unsurprising that they self-assemble via the hydrogen-bonded carboxylic dimer supramolecular synthon to afford an infinite diamondoid network. Each network possesses cavities that could accommodate a large roughly spherical guest, or guest aggregate, of roughly 12 Å in diameter. However, these cavities are filled by five independent networks that interpenetrate in such a way that the crystal structure is densely packed, and consequently, guest inclusion is precluded. As subsequent studies have revealed, interpenetration is a widespread phenomenon in diamondoid networks and occurs in many other organic and metal–organic structures that would otherwise have large cavities or channels. An interpenetrated diamondoid architecture is also exhibited by methanetetraacetic acid, for which the cavities generated are approximately 10 Å in diameter.[87] As would be expected, methanetetraacetic acid exhibits a lower degree of interpenetration: 3-fold. 2,6-dimethylidineadamantane-1,3,5,7-tetracarboxylic acid also forms a hydrogen-bonded diamondoid structure, but it exhibits a much lower degree of interpenetration

than its unsubstituted precursor. The 2-fold "double diamondoid" architecture is not as densely packed, and it can therefore act as a host and enclathrate guest molecules.[86]

Wuest demonstrated that the pyridone moiety also generates a hydrogen-bonded supramolecular synthon that is suitable for building extended arrays.[89,303,304] Remarkably, methanetetra(6-phenylethynyl-2-pyridone) exhibits a diamondoid network, 7-fold interpenetration, and cavities large enough to enclathrate butyric or valeric acid.[89] Wuest introduced the concept of "tectons" to describe molecules that inherently possess the molecular structure and intermolecular recognition features to predictably self-assemble into crystalline networks. This study was followed by studies that demonstrated that there are several other examples of diamondoid networks that can be sustained by the pyridone moiety.[305,306]

2. Modular Self-Assembly of Hydrogen-Bonded Diamondoid Networks

As discussed earlier, modular self-assembly relies upon two molecular components that are not individually capable of self-assembly and can be invoked
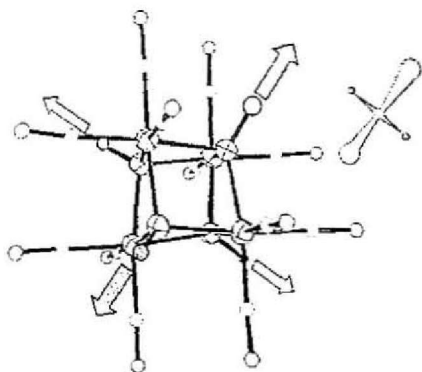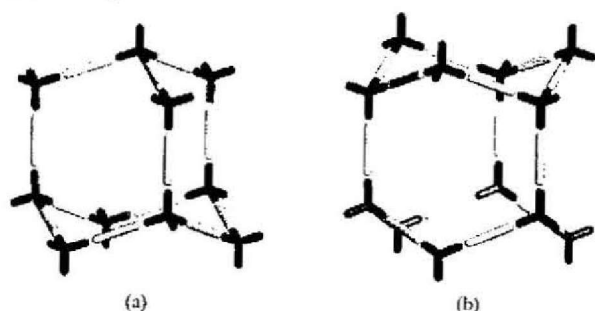
Figure 21. $[Mn(\mu_3\text{-OH})(CO)_3]_4$: a cubane-like cluster possessing perfect T_d symmetry that represents a prototypal example of a tetrahedral hydrogen-bond donor.

Scheme 16. Schematic Illustration of the Two Types of Diamondoid Architecture: (a) Cubic and (b) Hexagonal

(a)   (b)

Figure 22. Illustration of the crystal structure and diamondoid cavity generated in $[Mn(\mu_3\text{-OH})(CO)_3]_4 \cdot 2benzene$.

to understand coordination polymers or multiple-component hydrogen-bonded networks.[90] There are significant differences between the types of tetrahedral moiety that can sustain networks that have been self-assembled from a single component vs networks that have been self-assembled from multiple components. The most fundamental difference between the two types of structure is that the tetrahedral component that sustains single-component self-assembled architectures would ordinarily be able to sustain modular architectures and vice versa. In the case of the former, the tetrahedral moieties must be self-complementary and there is only one component necessary for self-assembly to occur. This means, for example, that both hydrogen-bond donors and hydrogen-bond acceptors must be present in the same molecule. In the case of the latter, the tetrahedral node must be either an acceptor or a donor of hydrogen bonds and the linker or spacer must be complementary. Both components are necessary, and there must be a 1:2 ratio in order for the diamondoid architecture to self-assemble. Scheme 16 illustrates the difference between the two types of diamondoid networks.

An example of a node that is suitable for modular self-assembly is the cubane cluster $[Mn(\mu_3\text{-OH})\text{-}(CO)_3]_4$,[307] which possesses perfect T_d symmetry and has four strong hydrogen-bond donors and no strong hydrogen-bond acceptors (Figure 21). This tetrahedral hydrogen-bond donor forms diamondoid cocrystals with a wide range of obvious and, in some cases, not so obvious spacer molecules. A "not so obvious"
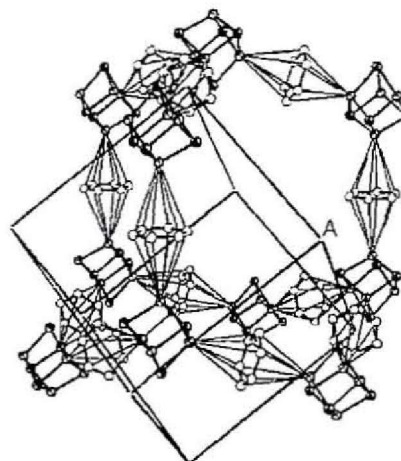
structure is that formed when $[Mn(\mu_3\text{-OH})(CO)_3]_4$ is cocrystallized with benzene.[308] A 2-fold diamondoid structure is sustained by OH$\cdots\pi$ hydrogen bonds, and the tetrahedral symmetry of the node is observed in the crystallographic sense since $[Mn(\mu_3\text{-OH})(CO)_3]_4 \cdot$ 2benzene crystallizes in the cubic space group Pn-$3m$ with $z = 2$. As revealed by Figure 22, which illustrates an adamantoid portion of the structure, a large cavity is generated and this facilitates interpenetration of a second diamondoid network.

The use of transition metals or transition-metal clusters to act as nodes for the modular self-assembly of diamondoid networks that are sustained by coordinate covalent bonds is also well established. Such architectures are of more than aesthetic appeal, and they have resulted in a class of compounds with interesting bulk and functional properties. Metal−organic diamondoid structures in which the spacer moiety has no center of inversion are predisposed to generate polar networks since there would not be an inherent center of inversion. Pyridine-4-carboxylic acid, isonicotinic acid, is such a ligand, and bis-(isonicotinato)zinc exists as a 3-fold diamondoid structure that is both thermally stable and inherently polar.[228] It exhibits SHG activity that is three times higher than the commercially relevant NLO material KDP.[309,310]

There are also supramolecular synthons that do not rely upon hydrogen bonds. In this context, N$\cdots$Br interactions were exploited to propagate a diamondoid network in the cocrystal formed by carbon tetrabromide and hexamethylenetetraaamine. This structure also represents a different but equally effective form of the modular approach: two tetrahedral nodes with one possessing donor functionality and the other acceptor functionality only. The structure of the cocrystal formed by carbon tetrabromide and hexamethylenetetraaamine exhibits 2-fold interpenetration and does not enclathrate solvent or guest.[311]

3. Other 3D Hydrogen-Bonded Networks

Although there are many examples of organic crystals that can be defined as 3D networks, few of

Scheme 17. Schematic Illustrating Five Supramolecular Synthons Possible for Pyromellitate Dianions
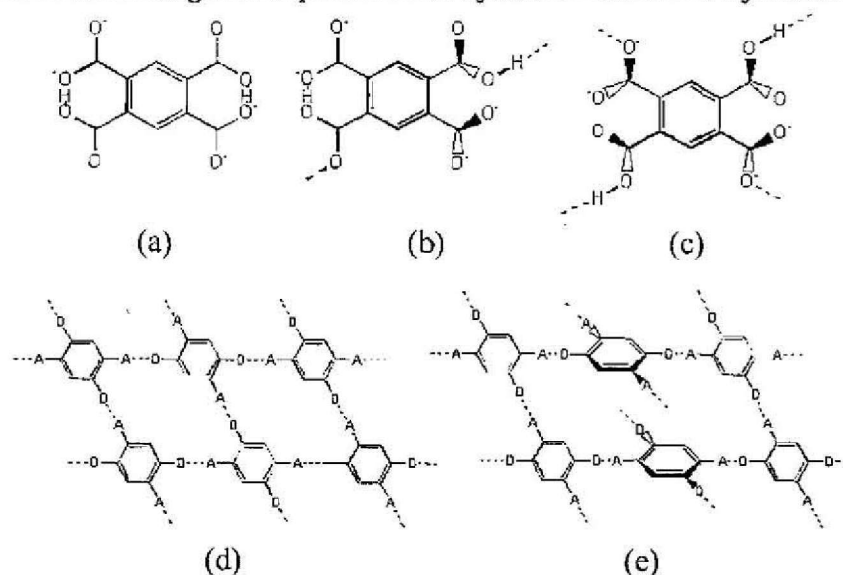
them are predictable or even rational in the same sense as diamondoid networks. Trimesic acid, H₃-TMA, is an interesting exception and was discussed earlier in the context of 2D structures. H₃TMA represents a prototypal molecule in the context of hydrogen bonding and generates extended structures when pure, partially deprotonated, in coordination polymers or in cocrystals. Anionic derivatives of H₃TMA self-assemble into honeycomb grids via O—H···O hydrogen bonds.[280–282,312,313] Pyromellitic acid, 1,2,4,5-benzenetetracarboxylic acid, H₄PMA, has been less widely explored than H₃TMA. It has been utilized as a ligand in coordination polymer networks,[294] and very few organic structures containing H₄PMA or its derivatives are known. We anticipated that doubly deprotonated H₄PMA would self-assemble via dicarboxylate hydrogen bonds to form 0D (two intramolecular hydrogen bonds), 1D (one intramolecular and one intermolecular hydrogen bond), or 2D/3D (two intermolecular hydrogen bonds) networks (Scheme 17). H₂PMA²⁻ anions exhibit all four of these supramolecular isomers depending upon the polymorph or the counterion.[314] The 3D structure occurs because H₂PMA²⁻ moieties orient in such a manner that they form hydrogen bonds to the next layer. The network can be described as a framework built from square building blocks that alternate parallel and perpendicular with respect to one another. This network can therefore be regarded as an organic analogue of NbO.[66]

It should be obvious that all 2D networks must, in the absence of solvent or intercalated guest, engage in noncovalent interactions with the layers above and below. The possibility of exploiting a combination of molecular recognition modes represents a particularly attractive approach to control crystal packing since it places no restrictions in terms of the type of chemical components that can be rationally incorporated into crystalline phases. In this context, Fowler and Lauher[19,315–320] illustrated how it is possible to use hydrogen bonding to control interactions between 1D networks, or á-networks, and to thereby yield

predictable 2D networks or α-networks. If the sheets are designed to be self-complementary in the third dimension, then a predictable 3D network or γ-network can result. Fowler and Lauher demonstrated not only that such a strategy is viable, but that it can offer a degree of control over stacking of layers such that the interlayer components are positioned within the limits of the topochemical principle. They were thereby able to effect solid-state reactions upon appropriate perturbation. When coupled with other advances in this context, including recent reports[17,19] that demonstrate how discrete aggregates may also afford components that are positioned within the topochemical boundaries, it should be clear that crystal engineering involving multiple types of molecular recognition offers significant implications for solid-state synthesis and solvent-free, green chemistry.

IV. Supramolecular Isomerism and Polymorphism

The existence of supramolecular isomerism might be seen as a problem from a design perspective since it necessarily implies that there will be superstructural diversity for a given molecular building block. However, there is another way to look at this matter. It is also possible to view supramolecular isomerism as an opportunity to gain a better fundamental understanding of the factors that influence crystal nucleation and growth. Such a linkage can be justified as follows. (1) If one invokes the concept of supramolecular isomerism, then it should become apparent that it represents a significant limitation on the number of possible superstructures (i.e., discrete structures or 1D, 2D, or 3D networks) that can occur for a given molecular building block. Therefore, one can invoke a study on supramolecular isomerism or polymorphism with the assumption that self-assembly means that there will only be a finite number of architectures that are feasible for a given molecular species. This assumption will be based upon crystals being the result of directional

Scheme 18. Schematic Illustration of the Six Supramolecular Isomers Reported for T-Shaped Nodes Linked by Linear Bifunctional Exodentate Ligands: (a) 1D Ladder, (b) 3D Lincoln Logs, (c) 2D Herringbone, (d) 2D Bilayer, (e) 2D Brick Wall, and (f) 3D Frame

(a)   (b)   (c)

(d)   (e)   (f)
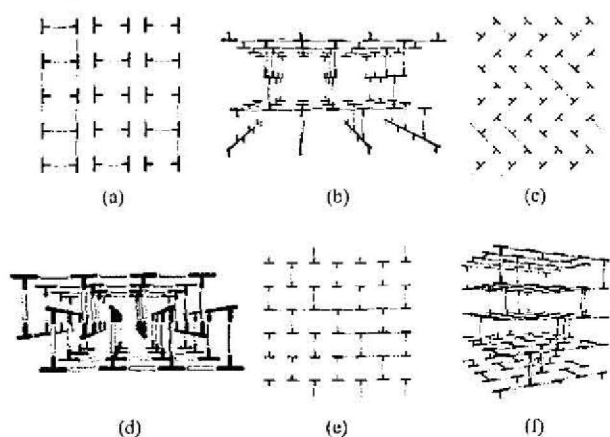
supramolecular synthons, the fundamental precept of crystal engineering. (2) The ability of the crystal engineer to design a molecular building block that is predisposed toward the formation of supramolecular isomers provides an ideal opportunity for design of supramolecular isomers and, perhaps more importantly, for learning how to control supramolecular isomers. At the very least, it will be possible to develop "recipes" that invoke crystallization conditions, templates, and/or solvents to favor or disfavor a particular supramolecular isomer.[321,322] (3) The concepts of self-assembly, crystal engineering, and networking provide clear implications for gaining a better fundamental understanding of polymorphism since polymorphism can be regarded as a subset of supramolecular isomerism. (4) It should be clear that to gain a better understanding of supramolecular isomerism and polymorphism, it is a requirement that full structural characterization of compounds be conducted. This means an in-depth analysis of crystal packing and intermolecular contacts as well as measurement of physical properties.

To illustrate the linkage between crystal engineering, supramolecular isomerism, and polymorphism, we shall consider three types of supramolecular isomerism and demonstrate how analogies can be readily drawn between coordination polymers and organic networks.

A. Structural Supramolecular Isomerism

That structural supramolecular isomerism can have profound implications for structure and properties is exemplified by the range of structures that has thus far been observed in coordination polymers that are generated by one of the simplest building blocks and stoichiometries: 1:1.5 stoichiometry, mer-metal, and linear spacer ligand. These building blocks can be regarded as being based upon self-assembly of T-shaped nodes. There already exists a surprisingly diverse range of structures that have been observed in this context. Scheme 18 illustrates the supramo-

lecular isomers that have thus far been observed: ladder[91,178] (A), brick wall[204] (B), 3D frame or "Lincoln Logs"[236,237] (C), bilayer[213] (D), herringbone[210] (E),[78,211,212] and another version of a 3D frame[177] (F). Three of the isomers A,[178] D,[213] and F[177] have been observed for the same asymmetric unit for metal = Co(NO$_3$)$_2$ and ligand = bipy, and the other three have been seen in similar compounds which use bipy or extended analogues as "spacer ligands".

The following points should be noted about such structures. (1) These compounds are not true polymorphs since guest or solvent molecules are present in the lattice. However, neither are they solvates in the conventional sense. (2) The diversity of network structures and hence bulk properties is remarkable. (3) None of these architectures occurs naturally in minerals. (4) The network structures themselves are entirely predictable based upon simple structural considerations. (5) Some of these structures can occur from the same building blocks under almost identical crystallization conditions.

It is possible to draw direct analogies with polymorphism in organic crystals. For example, a similar approach based upon networks can be used to analyze the packing in organic compounds. A recent paper highlighted this situation in the context of 2-amino-5-nitropyrimidine, a compound that exhibits three readily available polymorphs, all of which have distinct hydrogen-bonded networks.[323] Etter's study concerning carboxylic acids[88] and how they can self-assemble to form either head-to-tail chains or centrosymmetric dimers also illustrates how one can rationalize polymorphism based upon supramolecular isomers and networks.

In summary, it seems likely that use of appropriate templates or guest molecules facilitates recipes that can be used to reliably generate all supramolecular isomers that are possible for a given node. Therefore, one might assert that there are a finite number of superstructures possible for a given molecular moiety and that it will eventually be possible to determine the crystallization conditions under which each one will occur.

B. Conformational Supramolecular Isomerism

Flexibility in ligands can lead to subtle or dramatic changes in architecture. For example, 1,2-bis(pyridyl)ethane, bipy-eta, can readily adapt *gauche*- or *anti*-conformations. In the case of [Co(bipy-eta)$_{1.5}$-(NO$_3$)$_2$]$_n$, which contains a T-shaped node, infinite molecular ladders which contain six molecules of chloroform per cavity exist as the most commonly encountered architecture (Figure 23a).[186] In such a situation, all "spacer ligands" are necessarily *anti*. However, under certain crystallization conditions (e.g., solvent MeCN or dioxane), a bilayer architecture is obtained with two *anti*- and one *gauche*-spacer ligand per metal atom (Figure 23b).

The bilayer architecture can contain solvent molecules such as MeCN or can collapse on itself in the absence of solvent.[44] This more subtle form of supramolecular isomerism occurs if [Co(bipy-eta)$_{1.5}$-(NO$_3$)$_2$]$_n$ is crystallized in the absence of a suitable guest or solvent.[217] Figure 24 reveals how [Co(bipy-
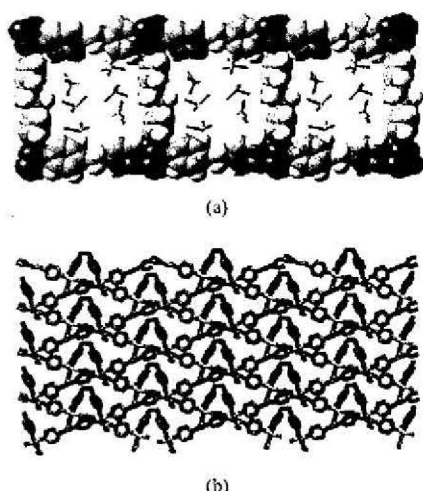
(a)

(b)

Figure 23. Illustrations of two structures observed for [Co-(bipy-eta)$_{1.5}$(NO$_3$)$_2$]: (a) ladder in which all bipy-eta ligands adapt an *anti*-orientation and (b) bilayer in which bipy-eta ligands adapt *anti*- and *gauche*-orientations in a 2:1 ratio.
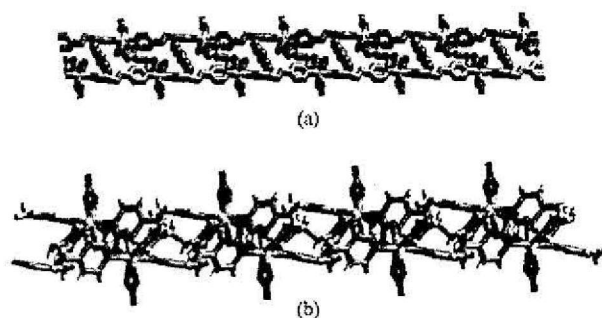

(a)

(b)

Figure 24. Illustrations of crystal structures of [Co(bipy-eta)$_{1.5}$(NO$_3$)$_2$] cocrystallized with (a) MeCN and (b) no solvent of crystallization. Note how the cavities collapse in the absence of the adsorbed solvent.

eta)$_{1.5}$(NO$_3$)$_2]_n$ collapses to close the cavity that exists when crystallized from MeCN.[44] Note the difference in torsion angles between the two compounds. A similar situation occurs in compounds based upon a longer bis-pyridyl ligand, 1,4-bis((4-pyridyl)methyl)-2,3,5,6-tetrafluorophenylene, **2**. When **2** is complexed to Cd to form compounds of formula [Cd(**2**)$_2$(NO$_3$)$_2$], three very different supramolecular isomers have been observed depending upon the nature of guests or templates: 1D chains, 2D sheets, and 3D diamondoid networks.[324]

A dramatic illustration of how conformational variability can influence crystal packing in organic compounds is illustrated by the compound 5-methyl-2-[(2-nitrophenyl)amino]-3-thiophenecarbonitile. This compound exists in at least six polymorphic phases. The primary difference between the six phases lies with the torsion angle between the thiophene moiety and the *o*-nitroaniline fragment, which varies from 21.7° to 104.7°.[55]

C. Catenane Supramolecular Isomerism

The existence of independent interpenetrating networks is surprisingly common if relatively large
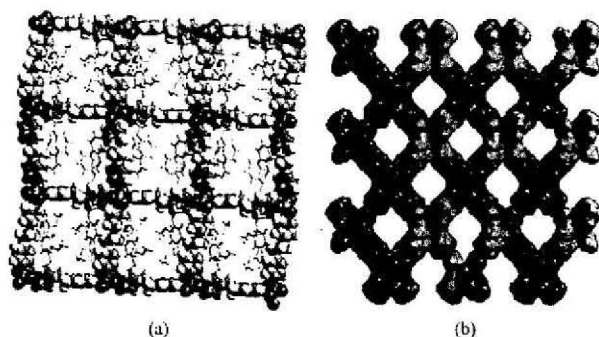

(a)   (b)

Figure 25. Illustrations of two crystal structures of the square grid coordination polymer [Ni(bipy-eta)$_2$(NO$_3$)$_2$]: (a) with included guest molecules and (b) interpenetrated networks.

cavities are generated within a network. A thorough review of this subject in the context of coordination polymers was recently published by Batten and Robson.[58] The existence of interpenetration has been regarded as a factor that mitigates strongly against the generation of stable open framework structures. However, it is becoming clear that appropriate use of templates can afford either open framework or interpenetrated structures for the same network. This is exemplified by the prototypal diamondoid and square grid networks Cd(CN)$_2$ and M(bipy)$_2$X$_2$. Both of these compounds have been prepared as interpenetrated and noninterpenetrated forms. Furthermore, some interpenetrated structures can also be regarded as open framework since if interpenetration will not necessarily afford close-packing. Interpenetrated structures can still contain channels large enough to hold, for example, aromatic guests. Such is the case for square grid networks based upon ligands such as bipy-eta. Figure 25 reveals how either open framework square grid or interpenetrated square grid structures can be readily generated for the same square grid network.[200] Both compounds contain square grids of formula [Ni(bipy-eta)$_2$(NO$_3$)]$_n$. As would be expected, the compound illustrated in Figure 25a, [Ni(bipy-eta)$_2$(NO$_3$)]$_n$, exhibits clay-like properties and can desorb and adsorb guests. Crystallinity is lost, but the square grid architecture retains its integrity below 220 °C. The interpenetrated analogue is illustrated in Figure 25b and is effectively a 3D architecture that is built by interpenetration of square grids. This compound has a more rigid structure than its noninterpenetrated form and behaves like a zeolitic solid rather than a clay-like solid. Both compounds are stable to loss of guest, but the former loses crystallinity upon loss of guest.

Organic networks are also capable of exhibiting interpenetration, and in this context H$_3$TMA represents a prototypal example. As discussed earlier, H$_3$TMA is predisposed to generate honeycomb sheets with large cavities. Three phases of H$_3$TMA have thus far been characterized. In two of these phases, one of which is pure H$_3$TMA, 3-fold interpenetration of the individual hexagonal cavities occurs.[282] In pure H$_3$TMA, the honeycomb networks are puckered in such a manner that small cavities are generated.[280] These cavities can hold small molecules, including
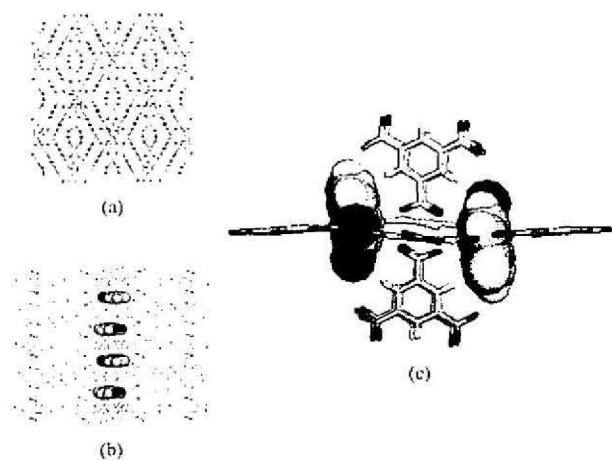
Figure 26. Illustration of the α-polymorph of BTC that illustrates how BTC can sustain the enclathration of *p*-nitroaniline: (a) view of the 10-fold interpenetrated puckered honeycomb networks, (b) view of a single BTC network with 3-fold interpenetration per cavity and incorporation of *p*-nitroaniline in "pockets", and (c) perspective view of two *p*-nitroanilines situated in a single cavity, surrounded by the three interpenetrating networks.

halogens[312] and *p*-nitroaniline.[325] The structure of the inclusion compound formed between H_3TMA and *p*-nitroaniline is illustrated in Figure 26. The other interpenetrated phase of H_3TMA contains flat sheets, and it therefore contains infinite 1D channels.[281] The noninterpenetrated phase of H_3TMA, illustrated in Figure 14, is formed when long-chain alkanes are used during the crystallization process.

A honeycomb network is also generated when H_3-TMA is cocrystallized with bipy. This structure exhibits interpenetration in 2D to form a novel carpet-like architecture.[283] However, the noninterpenetrated form remains to be isolated.

The results described above all suggest that interpenetration can be avoided if appropriate templates are used during the crystallization. It is therefore reasonable to see interpenetration as another example of supramolecular isomerism, one that can be controlled by use of guest or template molecules during crystallization.

V. Potential Applications

A considerable amount of research into understanding the nature and predictability of supramolecular synthons remains to be conducted. An enhanced database concerning supramolecular synthons in the broad context would also assist our fundamental understanding of solution chemistry and biochemistry. Nevertheless, it is clear that there are a number of applications of crystal engineering that could be realized in the short term. Several of these are summarized below. (1) From a supramolecular perspective, binary compounds represent an illustration of how one might exploit the modular approach to design new supermolecules, especially in the solid state. It is reasonable to assert that supramolecular synthesis of new classes of cocrystal and modular solid offers potential to increase the known range of crystalline materials by two or three orders of

magnitude and to facilitate combinatorial approaches to materials science. For example, if one were to only consider cocrystals that are sustained by hydrogen bonding, a wide range of compositions exists that remain to be explored. It is perhaps sobering to realize that, at least in principle, molecules that are deficient in hydrogen-bond acceptors are inherently prone to form supermolecules with molecules that contain excess hydrogen-bond acceptors. Even if one considered only simple examples such as pyridines, there are many permutations for formation of binary compounds. If one were to study, for example, 20 pyridines and 20 carboxylic acids, then one would expect 400 new binary compounds with predictable composition and structure. Such a strategy could be important in the context of supramolecular derivatives of drugs and functional materials (i.e., modification of bulk properties without changing the molecular structure of the active species) or they could serve as precursors to covalent products, including polymers. Such an approach has already been effective in formulation of polaroid film.[326] There also exists the possibility of rationalizing certain types of host–guest structures as being based upon topologically complementary networks.[241,243] Such compounds are also based upon self-assembly and might be prototypal for large numbers of related structures. (2) It is already established that solvent-free synthesis, green chemistry, offers many potential advantages, including cost and environmental benefits.[13,14] Cocrystallization of substrates and subsequently conducting reactions in the solid state offers the opportunity for very careful control over regio- and stereochemistry. It is also possible that supramolecular arrays could act as precursors to new classes of 2D and 3D covalent polymers.[327] (3) New classes of adsorbent, "organic and metal–organic clays and zeolites" represent an area in which considerable progress has already been made. Such compounds offer clear potential for the following: efficient, cost-effective alternatives to current methods of enantiomeric separations, new materials for separation of gases, liquids, and solutes, new industrial heterogeneous catalysts, new drug delivery matrixes (e.g., matrix for oral delivery of otherwise unstable drugs), a new generation of chemical sensors, and new storage matrixes for gases such as methane. Recent results indicate that synthetic metal–organic polymers can offer high levels of thermal stability and can supersede zeolites in terms of surface area and capacity for small guest molecules.[76,81] (4) The rational design of polar materials for use in materials science also represents an aspect of crystal engineering that has already provided promising developments. Unfortunately, in most organic crystals, antiparallel architectures predominate, thereby canceling dipoles of highly polarizable molecules and mitigating against optimization of bulk polarity. Fortunately, there now exists an extended range of modular, open framework organic and metal–organic solids. Many of these compounds contain architectures (e.g., square grid, honeycomb, octahedral) that favor incorporation of polar strands into channels, thereby reducing the driving force for

antiparallel alignment. Results obtained by the groups of Hollingsworth[328-332] and Hulliger et al.[333-340] suggest that such compounds, in particular channel-type inclusion compounds, hold considerable promise in the context of the design of solids that possess fine-tunable bulk polarity. Diamondoid networks also offer considerable potential in this context since tetrahedral nodes do not contain a center of inversion.[90] The recent results of Lin's group indicate that diamondoid networks can couple high thermal stability with high SHG activity.[228,229] (5) Metal−organic polymers offer considerable potential in the context of molecular magnetism, semiconductors, and conductors.[341-347] Once again, the possibility of design and fine-tuning becomes apparent when one develops structures with predictable architectures that are based upon paramagnetic metal ions. The presence of guest molecules can be a desirable feature as it would be expected to offer a degree of fine-tuning that is not inherently present in single-component compounds.

VI. Conclusions and Future Directions

"*The peasant who wants to harvest in his lifetime cannot wait for the ab initio theory of weather*", H. G. von Schnering (1981).

The fundamental precept of crystal engineering is that all information necessary for design of extended 1D, 2D, and 3D structures is already present at the molecular level in existing chemical species. Recent advances in our understanding of supramolecular chemistry and supramolecular synthons have been aided by the advent of CCD diffractometers coupled with ever more powerful visualization and analysis tools. It should therefore be unsurprising that control over supramolecular architectures, also known as molecular tectonics,[348] has advanced rapidly in recent years. That these tools are now routinely available means that an even more concerted and systematic approach to gaining an understanding of the subtle factors that control architectures in the solid state is feasible. The rational design of supramolecular structure necessarily relies upon invoking the concepts of self-assembly, in effect supramolecular synthesis, and exploits noncovalent forces as varied as the following: (1) hydrogen bonding, including both strong hydrogen bonding (e.g., O−H- - -O) and weak hydrogen bonding (e.g., C−H- - -O and even C−H- - -π), (2) coordinate covalent bonds (e.g., metal-organic polymers). (3) electrostatic and charge-transfer attractions, and (4) aromatic π-stacking interactions.

These principles of crystal engineering and supramolecular synthesis have thus far been used to design, isolate, and characterize a number of novel network structures that are prototypal because they are based upon modular components. However, these networks are typically based upon relatively small molecular components and the number and chemical type of components is typically restricted. It is in these two areas that there appears to be almost unlimited potential for supramolecular synthesis. In the context of coordination polymer networks, a recent review indicates how wide the range of chemi-

cal components and accessible network motifs has become.[215] However, the scale of these structures is such that cavities and channels are on the order of 10 Å and, to date, each cavity is identical. Careful selection of appropriate substrates or components and ever more control over crystal packing will offer the potential for rational design of an even more extensive array of modular (i.e., binary, ternary, or even higher order) structures than those that are currently available. In particular, judicious choice of secondary building units,[84] supermolecules, or biomolecules as templates and nodes should afford composite materials with nanoscale dimensions and cavities. The same is likely to be true concerning the rational development of structures that are based upon components that are at first glance incompatible. A number of examples of pure crystalline compounds that are based upon metal−organic polymers and metal oxide clusters have been reported in recent years.[197,289,349,350] Such composite materials would represent "uncharted territory", but they are a natural outgrowth of modular approaches to chemistry and now appear to be at hand. In essence, suprasupermolecular[351] synthesis in the solid state is likely to develop considerably further and, whereas prediction of crystal structures remains an elusive goal that will continue to be addressed, it does not preclude short-term applications of crystal engineering in a number of important areas. H. G. von Schnering's comments therefore seem particularly appropriate to summarize the current opportunities for crystal engineering and design.[352]

VII. References

(1) Maddox, J. *Nature* **1988**, *335*, 201.
(2) Feynman, R. *Eng. Sci.* **1960**, 22−36.
(3) Schmidt, G. M. J. *Pure Appl. Chem.* **1971**, *27*, 647−678.
(4) Lehn, J. M. *Pure Appl. Chem.* **1978**, *50*, 871−892.
(5) Lehn, J. M. *Supramolecular Chemistry: Concepts and Perspectives*; VCH: Weinheim, 1995.
(6) Dunitz, J. D. *Pure Appl. Chem.* **1991**, *63*, 177−185.
(7) Dunitz, J. D. *Perspectives in Supramolecular Chemistry*; Desiraju, G. R., Ed.; Wiley: New York, 1996; Vol. 2.
(8) Bernstein, J.; Davey, R. J.; Henck, J. O. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3441−3461.
(9) Dunitz, J. D.; Bernstein, J. *Acc. Chem. Res.* **1995**, *28*, 193−200.
(10) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1461−1494.
(11) Fan, J.; Whiteford, J. A.; Olenyuk, B.; Levin, M. D.; Stang, P. J.; Fleischer, E. B. *J. Am. Chem. Soc.* **1999**, *121*, 2741−2752.
(12) Rodriguez-Hornedo, N.; Murphy, D. *J. Pharm. Sci.* **1999**, *88*, 651−660.
(13) Tanaka, K.; Toda, F. *Chem. Rev.* **2000**, *100*, 1025−1074.
(14) Toda, F. *Acc. Chem. Res.* **1995**, *28*, 480−486.
(15) Metzger, J. O. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2975−2978.
(16) Loupy, A. *Top. Curr. Chem.* **1999**, *206*, 153−207.
(17) MacGillivray, L. R.; Reid, J. L.; Ripmeester, J. A. *J. Am. Chem. Soc.* **2000**, *122*, 7817−7818.
(18) Xiao, J.; Yang, M.; Lauher, J. W.; Fowler, F. W. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 2132−2135.
(19) Kane, J. J.; Liao, R. F.; Lauher, J. W.; Fowler, F. W. *J. Am. Chem. Soc.* **1995**, *117*, 12003−12004.
(20) Desiraju, G. R.; Gavezzotti, A. *Chem. Commun.* **1989**, 621−623.
(21) Desiraju, G. R. *Acc. Chem. Res.* **1991**, *24*, 290−296.
(22) Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311−2327.
(23) Etter, M. C. *J. Phys. Chem.* **1991**, *95*, 4601−4610.
(24) Etter, M. C.; MacDonald, J. C.; Bernstein, J. *Acta Crystallogr.* **1990**, *B46*, 256−262.
(25) Etter, M. C. *Acc. Chem. Res.* **1990**, *23*, 120−126.
(26) Allen, F. H.; Kennard, O. *Chem. Des. Autom. News* **1993**, *8*, 31−37.
(27) Cohen, M. D. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 386-393.
(28) Green, B. S.; Heller, L. *Science* **1974**, *185*, 525−527.

(29) Addadi, L.; Moradian, J.; Shay, E.; Maroudas, N. G.; Weiner, S. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 2732–2736.
(30) Addadi, L.; Weiner, S. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 4110–4114.
(31) Addadi, L.; Berkovitchyellin, Z.; Weissbuch, I.; Vanmil, J.; Shimon, L. J. W.; Lahav, M.; Leiserowitz, L. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 466–485.
(32) Addadi, L.; Vanmil, J.; Gati, E.; Lahav, M. *Origins Life Evol. Biosphere* **1981**, *11*, 107–118.
(33) Addadi, L.; Lahav, M. *J. Am. Chem. Soc.* **1979**, *101*, 2152–2156.
(34) Mann, S.; Archibald, D. D.; Didymus, J. M.; Douglas, T.; Heywood, B. R.; Meldrum, F. C.; Reeves, N. J. *Science* **1993**, *261*, 1286–1292.
(35) Mann, S.; Heywood, B. R.; Rajam, S.; Walker, J. B. A. *ACS Symp. Ser.* **1991**, *444*, 28–41.
(36) Jones, W.; Ramdas, S.; Theocharis, C. R.; Thomas, J. M.; Thomas, N. W. *J. Phys. Chem.* **1981**, *85*, 2594–2597.
(37) Thomas, J. M. *Philos. Trans. R. Soc. London, Ser. A* **1974**, *277*, 251–287.
(38) Davey, R. J.; Black, S. N.; Bromley, L. A.; Cottier, D.; Dobbs, B.; Rout, J. E. *Nature* **1991**, *353*, 549–550.
(39) Davey, R. J.; Mullin, J. W. *J. Cryst. Growth* **1974**, *26*, 45–51.
(40) Desiraju, G. R. *Crystal Engineering: the Design of Organic Solids*; Elsevier: Amsterdam, 1989.
(41) Gavezzotti, A. *Crystallogr. Rev.* **1998**, *7*, 5–121.
(42) Muller, A.; Krickemeyer, E.; Meyer, J.; Bogge, H.; Peters, F.; Plass, W.; Diemann, E.; Dillinger, S.; Nonnenbruch, F.; Randerath, M.; Menke, C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2122–2124.
(43) Gavezzotti, A. *Acc. Chem. Res.* **1994**, *27*, 309–314.
(44) Hennigar, T. L.; MacQuarrie, D. C.; Losier, P.; Rogers, R. D.; Zaworotko, M. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 972–973.
(45) Swift, J. A.; Pivovar, A. M.; Reynolds, A. M.; Ward, M. D. *J. Am. Chem. Soc.* **1998**, *120*, 5887–5894.
(46) Nangia, A.; Desiraju, G. R. *Chem. Commun.* **1999**, 605–606.
(47) Sarma, J. A. R. P.; Desiraju, G. R. Polymorphism and Pseudopolymorphism in Organic Crystals: a Cambridge Structural Database study. *Crystal Engineering: the design and application of functional solids*; Zaworotko, M. J., Seddon, K. R., Eds.; Kluwer: Dordrecht, 1999; pp 325–356.
(48) Braga, D.; Grepioni, F. *Chem. Soc. Rev.* **2000**, *29*, 229–238.
(49) Dunitz, J. D. *Acta Crystallogr.* **1995**, *B51*, 619–631.
(50) Threlfall, T. L. *Analyst* **1995**, *120*, 2435–2460.
(51) Masciocchi, N.; Ardizzoia, G. A.; Lamonica, G.; Moret, M.; Sironi, A. *Inorg. Chem.* **1997**, *36*, 449–454.
(52) Zerkowski, J. A.; MacDonald, J. C.; Whitesides, G. M. *Chem. Mater.* **1997**, *9*, 1933–1941.
(53) Chin, D. N.; Palmore, G. T. R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1999**, *121*, 2115–2122.
(54) McCrone, W. C. *Polymorphism in Physics and Chemistry of the Organic Solid-State*; Fox, D., Labes, M. M., Weisemberg, A., Eds.; Interscience: New York, 1965; p 726.
(55) Yu, L.; Stephenson, G. A.; Mitchell, C. A.; Bunnell, C. A.; Snorek, S. V.; Bowyer, J. J.; Borchardt, T. B.; Stowell, J. G.; Byrn, S. R. *J. Am. Chem. Soc.* **2000**, *122*, 585–591.
(56) Bernstein, J. *Organic Solid-State Chemistry*; Elsevier: Amsterdam, 1987; p 471.
(57) Bernstein, J.; Sarma, J. A. R. P.; Gavezzotti, A. *Chem. Phys. Lett.* **1990**, *174*, 361–368.
(58) Ball, P. *Nature* **1996**, *381*, 648–650.
(59) Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W. S.; Withersby, M. A.; Schroder, M. *Coord. Chem. Rev.* **1999**, *183*, 117–138.
(60) Lahav, M.; Leiserowitz, L. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2533–2536.
(61) Wen, R. W.; Bernal, I.; Fronczek, F. R. *J. Coord. Chem.* **1999**, *49*, 33–43.
(62) Cunningham, I. D.; Coles, S. J.; Hursthouse, M. B. *Chem. Commun.* **2000**, 61–62.
(63) Kostyanovsky, R. G.; Avdeenko, A. P.; Konovalova, S. A.; Kadorkina, G. K.; Prosyanik, A. V. *Mendeleev Commun.* **2000**, 16–18.
(64) Koshima, H.; Hayashi, E.; Matsuura, T. *Supramol. Chem.* **1999**, *11*, 57–66.
(65) Sakamoto, M. *Chem. Eur. J.* **1997**, *3*, 684–689.
(66) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Oxford University Press: Oxford, 1984.
(67) Wells, A. F. *Three-dimensional Nets and Polyhedra*; Wiley: New York, 1977.
(68) Robson, R.; Abrahams, B. F.; Batten, S. R.; Gable, R. W.; Hoskins, B. F.; Liu, J. P. *ACS Symp. Ser.* **1992**, *499*, 256–273.
(69) Abrahams, B. F.; Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1991**, *113*, 3606–3607.
(70) Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151–1152.
(71) Abrahams, B. F.; Hoskins, B. F.; Liu, J. P.; Robson, R. *J. Am. Chem. Soc.* **1991**, *113*, 3045–3051.
(72) Batten, S. R.; Hoskins, B. F.; Robson, R. *Chem. Commun.* **1991**, 445–447.
(73) Gable, R. W.; Hoskins, B. F.; Robson, R. *Chem. Commun.* **1990**, 762–763.
(74) Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546–1554.
(75) Abrahams, B. F.; Hoskins, B. F.; Robson, R. *Chem. Commun.* **1990**, 60–61.
(76) Noro, S.; Kitagawa, S.; Kondo, M.; Seki, K. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 2081–2084.
(77) Kondo, M.; Shimamura, M.; Noro, S.; Kimura, Y.; Uemura, K.; Kitagawa, S. *J. Solid State Chem.* **2000**, *152*, 113–119.
(78) Kondo, M.; Shimamura, M.; Noro, S.; Minakoshi, S.; Asami, A.; Seki, K.; Kitagawa, S. *Chem. Mater.* **2000**, *12*, 1288–1299.
(79) Kabir, M. K.; Miyazaki, N.; Kawata, S.; Adachi, K.; Kumagai, H.; Inoue, K.; Kitagawa, S.; Iijima, K.; Katada, M. *Coord. Chem. Rev.* **2000**, *198*, 157–169.
(80) Eddaoudi, M.; Li, H. L.; Yaghi, O. M. *J. Am. Chem. Soc.* **2000**, *122*, 1391–1397.
(81) Li, H.; Eddaoudi, M.; O'Keefe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276–279.
(82) Xu, Z. F.; Moore, J. S. *Acta Polym.* **1994**, *45*, 83–87.
(83) Li, H. L.; Laine, A.; O'Keefe, M.; Yaghi, O. M. *Science* **1999**, *283*, 1145–1147.
(84) Yaghi, O. M.; Li, H. L.; Davis, C.; Richardson, D.; Groy, T. L. *Acc. Chem. Res.* **1998**, *31*, 474–484.
(85) Ermer, O.; Lindenberg, L. *Helv. Chim. Acta* **1988**, *71*, 1084–1093.
(86) Ermer, O. *J. Am. Chem. Soc.* **1988**, *110*, 3747–3754.
(87) Ermer, O.; Eling, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 829–833.
(88) Frankenbach, G. M.; Etter, M. C. *Chem. Mater.* **1992**, *4*, 272–278.
(89) Su, D.; Wang, X.; Simard, M.; Wuest, J. D. *Supramol. Chem.* **1995**, *6*, 171–178.
(90) Zaworotko, M. J. *Chem. Soc. Rev.* **1994**, *23*, 283–288.
(91) Withersby, M. A.; Blake, A. J.; Champness, N. R.; Cooke, P. A.; Hubberstey, P.; Li, W. S.; Schroder, M. *Inorg. Chem.* **1999**, *38*, 2259–2266.
(92) Keefe, M. H.; Slone, R. V.; Hupp, J. T.; Czaplewski, K. F.; Snurr, R. Q.; Stern, C. L. *Langmuir* **2000**, *16*, 3964–3970.
(93) Branden, C.; Tooze, J. *Introduction to Protein Structure*; Garland: New York, 1999.
(94) Belanger, S.; Keefe, M. H.; Welch, J. L.; Hupp, J. T. *Coord. Chem. Rev.* **1999**, *192*, 29–45.
(95) Belanger, S.; Hupp, J. T. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2222–2224.
(96) Belanger, S.; Hupp, J. T.; Stern, C. L.; Slone, R. V.; Watson, D. F.; Carrell, T. G. *J. Am. Chem. Soc.* **1999**, *121*, 557–563.
(97) Benkstein, K. D.; Hupp, J. T.; Stern, C. L. *J. Am. Chem. Soc.* **1998**, *120*, 12982–12983.
(98) Slone, R. V.; Benkstein, K. D.; Belanger, S.; Hupp, J. T.; Guzel, I. A.; Rheingold, A. L. *Coord. Chem. Rev.* **1998**, *171*, 221–243.
(99) Kim, S.; Smith, T. J.; Chapman, M. S.; Rossmann, M. G.; Pevear, D. C.; Dutko, F. J.; Felock, P. J.; Diana, G. D.; McKinlay, M. A. *J. Mol. Biol.* **1989**, *210*, 91–111.
(100) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502–518.
(101) Slone, R. V.; Hupp, J. T. *Inorg. Chem.* **1997**, *36*, 5422–5423.
(102) Manna, J.; Kuehl, C. J.; Whiteford, J. A.; Stang, P. J.; Muddiman, D. C.; Hofstadler, S. A.; Smith, R. D. *J. Am. Chem. Soc.* **1997**, *119*, 11611–11619.
(103) Cao, D. H.; Chen, K. C.; Fan, J.; Manna, J.; Olenyuk, B.; Whiteford, J. A.; Stang, P. J. *Pure Appl. Chem.* **1997**, *69*, 1979–1986.
(104) Olenyuk, B.; Whiteford, J. A.; Stang, P. J. *J. Am. Chem. Soc.* **1996**, *118*, 8, 8221–8230.
(105) Fujita, M.; Ogura, G. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1471–1482.
(106) Fujita, M.; Sasaki, O.; Mitsuhashi, T.; Fujita, T.; Yazaki, J.; Yamaguchi, K.; Ogura, K. *Chem. Commun.* **1996**, 1535–1536.
(107) Stang, P. J.; Olenyuk, B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 732–736.
(108) Whitesell, J. K.; Davis, R. E.; Wong, M. S.; Chang, N. L. *J. Am. Chem. Soc.* **1994**, *116*, 523–527.
(109) Yoshizawa, M.; Kusukawa, T.; Fujita, M.; Yamaguchi, K. *J. Am. Chem. Soc.* **2000**, *122*, 6311–6312.
(110) MacGillivray, L. R.; Atwood, J. L. *J. Solid State Chem.* **2000**, *152*, 199–210.
(111) Muller, A.; Shah, S. Q. N.; Bogge, H.; Schmidtmann, M.; Kogerler, P.; Hauptfleisch, B.; Leiding, S.; Wittler, K. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 1614–1616.
(112) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853–907.
(113) Sakamoto, S.; Fujita, M.; Kim, K.; Yamaguchi, K. *Tetrahedron* **2000**, *56*, 955–964.
(114) Caulder, D. L.; Raymond, K. N. *Acc. Chem. Res.* **1999**, *32*, 975–982.
(115) Olenyuk, B.; Levin, M. D.; Whiteford, J. A.; Shield, J. E.; Stang, P. J. *J. Am. Chem. Soc.* **1999**, *121*, 10434–10435.

(116) Orr, G. W.; Barbour, L. J.; Atwood, J. L. *Science* **1999**, *285*, 1049−1052.
(117) MacGillivray, L. R.; Atwood, J. L. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1019−1034.
(118) Takeda, N.; Umemoto, K.; Yamaguchi, K.; Fujita, M. *Nature* **1999**, *398*, 794−796.
(119) Barbour, L. J.; Orr, G. W.; Atwood, J. L. *Nature* **1998**, *393*, 671−673.
(120) Stang, P. J. *Chem. Eur. J.* **1998**, *4*, 19−27.
(121) MacGillivray, L. R.; Atwood, J. L. *Nature* **1997**, *389*, 469−472.
(122) Conn, M. M.; Rebek, J. *Chem. Rev.* **1997**, *97*, 1647−1668.
(123) Hartshorn, C. M.; Steel, P. J. *Chem. Commun.* **1997**, 541−542.
(124) Muller, A.; Reuter, H.; Dillinger, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2328−2361.
(125) Fujita, M.; Oguro, D.; Miyazawa, M.; Oka, H.; Yamaguchi, K.; Ogura, K. *Nature* **1995**, *378*, 469−471.
(126) Muller, A.; Hovemeier, K.; Krickemeyer, E.; Bogge, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 779−781.
(127) Zhang, Y. W.; Seeman, N. C. *J. Am. Chem. Soc.* **1994**, *116*, 1661−1669.
(128) Meier, W. M.; Olson, D. H. *Atlas of Zeolite Structure Types*; Butterworth-Heinemann: Boston, 1992.
(129) Acharya, R.; Fry, E.; Stuart, D.; Fox, G.; Rowlands, D.; Brown, F. *Nature* **1989**, *337*, 709−716.
(130) Luo, M.; Vriend, G.; Kamer, G.; Minor, I.; Arnold, E.; Rossmann, M. G.; Boege, U.; Scraba, D. G.; Duke, G. M.; Palmenberg, A. C. *Science* **1987**, *235*, 182−191.
(131) Hogle, J. M.; Chow, M.; Filman, D. J. *Science* **1985**, *229*, 1358−1365.
(132) Proulxcurry, P. M.; Chasteen, N. D. *Coord. Chem. Rev.* **1995**, *144*, 347−368.
(133) Wenninger, M. J. *Polyhedron Models*; Cambridge University Press: Cambridge, 1989.
(134) Swiegers, G. F.; Malefetse, J. *Chem. Rev.* **2000**, *100*, 3483−3537.
(135) Slone, R. V.; Yoon, D. I.; Calhoun, R. M.; Hupp, J. T. *J. Am. Chem. Soc.* **1995**, *117*, 11813−11814.
(136) Cernak, J.; Abboud, K. A. *Acta Crystallogr.* **2000**, *C56*, 783−785.
(137) Colacio, E.; Ghazi, M.; Kivekas, R.; Klinga, M.; Lloret, F.; Moreno, J. M. *Inorg. Chem.* **2000**, *39*, 2770−2776.
(138) Guo, G. C.; Wang, Q. M.; Mak, T. C. W. *Inorg. Chem. Commun.* **2000**, *3*, 313−315.
(139) Abrahams, B. F.; Lu, K. D.; Moubaraki, B.; Murray, K. S.; Robson, R. *Dalton Trans.* **2000**, 1793−1797.
(140) Dong, Y. B.; Smith, M. D.; Zur Loye, H. C. *Inorg. Chem.* **2000**, *39*, 1943−1949.
(141) Colacio, E.; Dominguez-Vera, J. M.; Ghazi, M.; Kivekas, R.; Moreno, J. M.; Pajunen, A. *Dalton Trans.* **2000**, 505−509.
(142) Maekawa, M.; Sugimoto, K.; Kuroda-Sowa, T.; Suenaga, Y.; Munakata, M. *Dalton Trans.* **1999**, 4357−4362.
(143) Colacio, E.; Dominguez-Vera, J. M.; Ghazi, M.; Kivekas, R.; Klinga, M.; Moreno, J. M. *Eur. J. Inorg. Chem.* **1999**, 441−445.
(144) Mimura, M.; Matsuo, T.; Nakashima, T.; Matsumoto, N. *Inorg. Chem.* **1998**, *37*, 3553−3560.
(145) Sun, Z. M.; Gantzel, P. K.; Hendrickson, D. N. *Polyhedron* **1998**, *17*, 1511−1516.
(146) Stocker, F. B.; Troester, M. A.; Britton, D. *Inorg. Chem.* **1996**, *35*, 3145−3153.
(147) Ellis, W. W.; Schmitz, M.; Arif, A. A.; Stang, P. J. *Inorg. Chem.* **2000**, *39*, 2547−2557.
(148) Hong, M. C.; Su, W. P.; Cao, R.; Fujita, M.; Lu, J. X. *Chem. Eur. J.* **2000**, *6*, 427−431.
(149) Ranford, J. D.; Vittal, J. J.; Wu, D. Q.; Yang, X. D. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3498−3501.
(150) Jaunky, W.; Hosseini, M. W.; Planeix, J. M.; De Cian, A.; Kyritsakas, N.; Fischer, J. *Chem. Commun.* **1999**, 2313−2314.
(151) Saalfrank, R. W.; Maid, H.; Hampel, F.; Peters, K. *Eur. J. Inorg. Chem.* **1999**, 1859−1867.
(152) Mamula, O.; Von Zelewsky, A.; Bark, T.; Bernardinelli, G. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2945−2948.
(153) Ezuhara, T.; Endo, K.; Aoyama, Y. *J. Am. Chem. Soc.* **1999**, *121*, 1, 3279−3283.
(154) Biradha, K.; Seward, C.; Zaworotko, M. J. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 492−495.
(155) Kaes, C.; Hosseini, M. W.; Rickard, C. E. F.; Skelton, B. W.; White, A. H. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 920−922.
(156) Whang, D.; Heo, J.; Kim, C. A.; Kim, K. *Chem. Commun.* **1997**, 2361−2362.
(157) Psillakis, E.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D. *Dalton Trans.* **1997**, 1645−1651.
(158) Withersby, M. A.; Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W. S.; Schroder, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2327−2329.
(159) Blake, A. J.; Champness, N. R.; Khlobystov, A. N.; Parsons, S.; Schroder, M. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 2317−2320.
(160) Hardie, R. J.; Godfrey, P. D.; Raston, C. L. *Chem. Eur. J.* **1999**, *5*, 1828−1833.
(161) Katz, T. J. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 1921−1923.

(162) Corbin, P. S.; Zimmerman, S. C. *J. Am. Chem. Soc.* **2000**, *122*, 3779−3780.
(163) Masciocchi, N.; Ardizzoia, G. A.; Lamonica, G.; Maspero, A.; Sironi, A. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3366−3369.
(164) Bowyer, P. K.; Porter, K. A.; Rae, A. D.; Willis, A. C.; Wild, S. B. *Chem. Commun.* **1998**, 1153−1154.
(165) Rowan, A. E.; Nolte, R. J. M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 63−68.
(166) Wu, B.; Zhang, W. J.; Yu, S. Y.; Wu, X. T. *Dalton Trans.* **1997**, 1795−1796.
(167) Pecaut, J.; Lefur, Y.; Masse, R. *Acta Crystallogr.* **1993**, *B49*, 535−541.
(168) Etter, M. C.; Huang, K. S. *Chem. Mater.* **1992**, *4*, 824−827.
(169) Panunto, T. W.; Urbanczyklipkowska, Z.; Johnson, R.; Etter, M. C. *J. Am. Chem. Soc.* **1987**, *109*, 7786−7797.
(170) Gorbitz, C. H.; Etter, M. C. *J. Chem. Soc., Perkin Trans. 2* **1992**, 131−135.
(171) Leiserowitz, L. *Acta Crystallogr.* **1976**, *B32*, 775−802.
(172) Melendez, R.; Robinson, F.; Zaworotko, M. J. *Supramol. Chem.* **1996**, *7*, 275−293.
(173) Pepinsky, R.; Vedam, K. *Phys. Rev. A* **1960**, *117*, 1502−1503.
(174) Pepinsky, R.; Vedam, K.; Hoshino, S.; Okaya, Y. *Phys. Rev. A* **1958**, *111*, 1508−1510.
(175) Payan, F.; Haser, R. *Acta Crystallogr.* **1976**, *B32*, 1875−1879.
(176) Swift, J. A.; Ward, M. D. *Chem. Mater.* **2000**, *12*, 1501−1504.
(177) Gudbjartson, H.; Biradha, K.; Poirier, K. M.; Zaworotko, M. J. *J. Am. Chem. Soc.* **1999**, *121*, 2599−2600.
(178) Fujita, M.; Kwon, Y. J.; Sasaki, O.; Yamaguchi, K.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 7287−7288.
(179) Min, K. S.; Suh, M. P. *J. Solid State Chem.* **2000**, *152*, 183−190.
(180) Carlucci, L.; Ciani, G.; Proserpio, D. M. *Dalton Trans.* **1999**, 1799−1804.
(181) Liu, C. M.; You, X. Z.; Chen, W. *J. Coord. Chem.* **1998**, *46*, 183−191.
(182) Carlucci, L.; Ciani, G.; Proserpio, D. M. *Chem. Commun.* **1999**, 449−450.
(183) Aakeroy, C. B.; Beatty, A. M. *Cryst. Eng.* **1998**, *1*, 39−49.
(184) Fujita, M.; Sasaki, O.; Watanabe, K. Y.; Ogura, K.; Yamaguchi, K. *New J. Chem.* **1998**, *22*, 189−191.
(185) Blake, A. J.; Champness, N. R.; Khlobystov, A.; Lemenovskii, D. A.; Li, W. S.; Schroder, M. *Chem. Commun.* **1997**, 2027−2028.
(186) Losier, P.; Zaworotko, M. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2779−2782.
(187) Nishikiori, S.; Iwamoto, T. *Inorg. Chem.* **1986**, *25*, 788−794.
(188) Nishikiori, S.; Iwamoto, T. *J. Inclusion Phenom.* **1984**, *2*, 341−349.
(189) Nishikiori, S.; Iwamoto, T. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3246−3252.
(190) Miyoshi, T.; Iwamoto, T.; Sasaki, Y. *Inorg. Chim. Acta* **1972**, *6*, 59−64.
(191) Batten, S. R.; Hoskins, B. F.; Robson, R. *New J. Chem.* **1998**, *22*, 173−175.
(192) Abrahams, B. F.; Hardie, M. J.; Hoskins, B. F.; Robson, R.; Sutherland, E. E. *Chem. Commun.* **1994**, 1049−1050.
(193) Groeneman, R. H.; MacGillivray, L. R.; Atwood, J. L. *Chem. Commun.* **1998**, 2735−2736.
(194) Aoyagi, M.; Biradha, K.; Fujita, M. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1369−1373.
(195) Subramanian, S.; Zaworotko, M. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2127−2129.
(196) Gable, R. W.; Hoskins, B. F.; Robson, R. *Chem. Commun.* **1990**, 1677−1678.
(197) Hagrman, D.; Hammond, R. P.; Haushalter, R.; Zubieta, J. *Chem. Mater.* **1998**, *10*, 2091−2100.
(198) Lu, J.; Paliwala, T.; Lim, S. C.; Yu, C.; Niu, T. Y.; Jacobson, A. J. *Inorg. Chem.* **1997**, *36*, 923−929.
(199) MacGillivray, L. R.; Groeneman, R. H.; Atwood, J. L. *J. Am. Chem. Soc.* **1998**, *120*, 2676−2677.
(200) Park, S. H.; Kim, K. M.; Lee, S.; Jung, O. S. *Bull. Korean Chem. Soc.* **1998**, *19*, 79−82.
(201) Moulton, B.; Zaworotko, M. J. *Rational Design of Polar Solids. Crystal Engineering: From Molecules and Crystals to Materials*; Braga, D., Ed.; Kluwer: Dordrecht, 1999; pp 311−330.
(202) Kumar, R. K.; Goldberg, I. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3027−3030.
(203) Biradha, K.; Fujita, M. *Chem. Commun.* **2001**, 15−16.
(204) Dong, Y. B.; Smith, M. D.; Layland, R. C.; Zur Loye, H. C. *Chem. Mater.* **2000**, *12*, 1156−1161.
(205) Sharma, C. V. K.; Rogers, R. D. *Cryst. Eng.* **1998**, *1*, 19−38.
(206) Kondo, M.; Asami, A.; Fujimoto, K.; Noro, S.; Kitagawa, S.; Ishii, T.; Matsuzaka, H. *Int. J. Inorg. Mater.* **1999**, *1*, 73−75.
(207) Dong, Y. B.; Smith, M. D.; Layland, R. C.; Zur Loye, H. C. *Dalton Trans.* **2000**, 775−780.
(208) Carlucci, L.; Ciani, G.; Proserpio, D. M. *New J. Chem.* **1998**, *22*, 1319−1321.
(209) Choi, H. J.; Suh, M. P. *J. Am. Chem. Soc.* **1998**, *120*, 10622−10628.

(210) Masse, R.; Nicoud, J. F.; Bagieu-Beucher, M.; Bourgogne, C. *Chem. Phys.* **1999**, *245*, 365–375.
(211) Withersby, M. A.; Blake, A. J.; Champness, N. R.; Cooke, P. A.; Hubberstey, P.; Schroder, M. *New J. Chem.* **1999**, *23*, 573–575.
(212) Dong, Y. B.; Layland, R. C.; Pschirer, N. G.; Smith, M. D.; Bunz, U. H. F.; Zur Loye, H. C. *Chem. Mater.* **1999**, *11*, 1413–1415.
(213) Power, K. N.; Hennigar, T. L.; Zaworotko, M. J. *New J. Chem.* **1998**, *22*, 177–181.
(214) Rujiwatra, A.; Kepert, C. J.; Rosseinsky, M. J. *Chem. Commun.* **1999**, 2307–2308.
(215) Kitagawa, S.; Kondo, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1739–1753.
(216) Kepert, C. J.; Rosseinsky, M. J. *Chem. Commun.* **1999**, 375–376.
(217) Atencio, R.; Biradha, K.; Hennigar, T. L.; Poirier, K. M.; Power, K. N.; Seward, C. M.; White, N. S.; Zaworotko, M. J. *Cryst. Eng.* **1998**, *1*, 203-212.
(218) MacGillivray, L. R.; Subramanian, S.; Zaworotko, M. J. *Chem. Commun.* **1994**, 1325–1326.
(219) Johnson, D. W.; Xu, J. D.; Saalfrank, R. W.; Raymond, K. N. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2882–2885.
(220) Abrahams, B. F.; Egan, S. J.; Robson, R. *J. Am. Chem. Soc.* **1999**, *121*, 3535–3536.
(221) Bruckner, C.; Powers, R. E.; Raymond, K. N. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1837–1839.
(222) Olenyuk, B.; Whiteford, J. A.; Fechtenkotter, A.; Stang, P. J. *Nature* **1999**, *398*, 796–799.
(223) Stang, P. J.; Olenyuk, B.; Muddiman, D. C.; Smith, R. D. *Organometallics* **1997**, *16*, 3094–3096.
(224) Yu, S. Y.; Kusukawa, T.; Biradha, K.; Fujita, M. *J. Am. Chem. Soc.* **2000**, *122*, 2665–2666.
(225) Fujita, M. *Chem. Soc. Rev.* **1998**, *27*, 417–425.
(226) Otieno, T.; Rettig, S. J.; Thompson, R. C.; Trotter, J. *Inorg. Chem.* **1993**, *32*, 1607–1611.
(227) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *Chem. Commun.* **1994**, 2755–2756.
(228) Evans, O. R.; Xiong, R. G.; Wang, Z. Y.; Wong, G. K.; Lin, W. B. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 536–538.
(229) Evans, O. R.; Wang, Z. Y.; Xiong, R. G.; Foxman, B. M.; Lin, W. B. *Inorg. Chem.* **1999**, *38*, 2969–2973.
(230) Lopez, S.; Kahraman, M.; Harmata, M.; Keller, S. W. *Inorg. Chem.* **1997**, *36*, 6138–6140.
(231) Hirsch, K. A.; Venkataraman, D.; Wilson, S. R.; Moore, J. S.; Lee, S. *Chem. Commun.* **1995**, 2199–2200.
(232) Yaghi, O. M.; Li, G. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 207–209.
(233) Sinzger, K.; Hunig, S.; Jopp, M.; Bauer, D.; Bietsch, W.; Von Schutz, J. U.; Wolf, H. C.; Kremer, R. K.; Metzenthin, T.; Bau, R.; Khan, S. I.; Lindbaum, A.; Lengauer, C. L.; Tillmanns, E. *J. Am. Chem. Soc.* **1993**, *115*, 7696–7705.
(234) Keggin, J. F. *Nature* **1936**, *137*, 577.
(235) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1895–1898.
(236) Robinson, F.; Zaworotko, M. J. *Chem. Commun.* **1995**, 2413–2414.
(237) Yaghi, O. M.; Li, H. L. *J. Am. Chem. Soc.* **1996**, *118*, 295–296.
(238) Holman, K. T.; Ward, M. D. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 1653–1656.
(239) Evans, C. C.; Sukarto, L.; Ward, M. D. *J. Am. Chem. Soc.* **1999**, *121*, 320–325.
(240) Swift, J. A.; Reynolds, A. M.; Ward, M. D. *Chem. Mater.* **1998**, *10*, 0, 4159–4168.
(241) Biradha, K.; Domasevitch, K. V.; Moulton, B.; Seward, C.; Zaworotko, M. J. *Chem. Commun.* **1999**, 1327–1328.
(242) Biradha, K.; Domasevitch, K. V.; Hogg, C.; Moulton, B.; Power, K. N.; Zaworotko, M. J. *Cryst. Eng.* **1999**, *2*, 37–45.
(243) Biradha, K.; Mondal, A.; Moulton, B.; Zaworotko, M. J. *Dalton Trans.* **2000**, *21*, 3837–3844.
(244) Soma, T.; Iwamoto, T. *Acta Crystallogr.* **1996**, *C52*, 1200–1203.
(245) Atencio, R.; Domasevitch, K. V.; Zaworotko, M. J. *Cryst. Eng.* **2000**, *3*, 63–69.
(246) Steiner, T.; Desiraju, G. R. *Chem. Commun.* **1998**, 891–892.
(247) Langley, P. J.; Hulliger, J.; Thalmattam, R.; Desiraju, G. R. *New J. Chem.* **1998**, *22*, 1307–1309.
(248) Steiner, T.; Tamm, M. *J. Organomet. Chem.* **1998**, *570*, 235–239.
(249) Steiner, T.; Lutz, B.; Van Der Maas, J.; Schreurs, A. M. M.; Kroon, J.; Tamm, M. *Chem. Commun.* **1998**, 171–172.
(250) Madhavi, N. N. L.; Katz, A. K.; Carrell, H. L.; Nangia, A.; Desiraju, G. R. *Chem. Commun.* **1997**, 2249.
(251) Steiner, T. *Chem. Commun.* **1997**, 727–734.
(252) Desiraju, G. R.; Gavezzotti, A. *Acta Crystallogr.* **1989**, *B45*, 473–482.
(253) Gavezzotti, A.; Desiraju, G. R. *Acta Crystallogr.* **1988**, *B44*, 427–434.
(254) Pedireddi, V. R.; Reddy, D. S.; Goud, B. S.; Craig, D. C.; Rae, A. D.; Desiraju, G. R. *J. Chem. Soc., Perkin Trans. 2* **1994**, 2353–2360.
(255) Desiraju, G. R.; Parthasarathy, R. *J. Am. Chem. Soc.* **1989**, *111*, 8725–8726.
(256) Broder, C. K.; Howard, J. A. K.; Keen, D. A.; Wilson, C. C.; Allen, F. H.; Jetti, R. K. R.; Nangia, A.; Desiraju, G. R. *Acta Crystallogr.* **2000**, *56*, 1080–1084.
(257) Aakeroy, C. B. *Acta Crystallogr.* **1997**, *B53*, 569–586.
(258) Aakeroy, C. B.; Seddon, K. R. *Chem. Soc. Rev.* **1993**, *22*, 397–407.
(259) Subramanian, S.; Zaworotko, M. J. *Coord. Chem. Rev.* **1994**, *137*, 357–401.
(260) Burrows, A. D.; Chan, C. W.; Chowdhry, M. M.; McGrady, J. E.; Mingos, D. M. P. *Chem. Soc. Rev.* **1995**, *24*, 329–339.
(261) Russell, V. A.; Ward, M. D. *Chem. Mater.* **1996**, *8*, 1654–1666.
(262) Rivas, J. C. M.; Brammer, L. *Coord. Chem. Rev.* **1999**, *183*, 43–80.
(263) Ashton, P. R.; Fyfe, M. C. T.; Hickingbottom, S. K.; Menzer, S.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **1998**, *4*, 577–589.
(264) Melendez, R. E. and Hamilton, A. D. *Hydrogen-Bonded Ribbons, Tapes and Sheets as Motifs for Crystal Engineering*; **1998**; pp 97–129.
(265) Lommerse, J. P. M.; Motherwell, W. D. S.; Ammon, H. L.; Dunitz, J. D.; Gavezzotti, A.; Hofmann, D. W. M.; Leusen, F. J. J.; Mooij, W. T. M.; Price, S. L.; Schweizer, B.; Schmidt, M. U.; Van Eijck, B. P.; Verwer, P.; Williams, D. E. *Acta Crystallogr.* **2000**, *56*, 697–714.
(266) Bailey, M.; Brown, C. J. *Acta Crystallogr.* **1967**, *22*, 387–391.
(267) Alcala, R.; Martinez.s *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *B 28*, 1671–1679.
(268) Yang, J.; Marendaz, J. L.; Geib, S. J.; Hamilton, A. D. *Tetrahedron Lett.* **1994**, *35*, 3665–3668.
(269) Valiyaveettil, S.; Mullen, K. *New J. Chem.* **1998**, *22*, 89–95.
(270) Whitesides, G. M.; Simanek, E. E.; Mathias, J. P.; Seto, C. T.; Chin, D. N.; Mammen, M.; Gordon, D. M. *Acc. Chem. Res.* **1995**, *28*, 37–44.
(271) Zerkowski, J. A.; Seto, C. T.; Whitesides, G. M. *J. Am. Chem. Soc.* **1992**, *114*, 5473–5475.
(272) Mathias, J. P.; Simanek, E. E.; Zerkowski, J. A.; Seto, C. T.; Whitesides, G. M. *J. Am. Chem. Soc.* **1994**, *116*, 4316–4325.
(273) Archer, E. A.; Gong, H. G.; Krische, M. J. *Tetrahedron* **2001**, *57*, 1139–1159.
(274) Simanek, E. E.; Mammen, M.; Gordon, D. M.; Chin, D.; Mathias, J. P.; Seto, C. T.; Whitesides, G. M. *Tetrahedron* **1995**, *51*, 607–619.
(275) Seto, C. T.; Whitesides, G. M. *J. Am. Chem. Soc.* **1993**, *115*, 905–916.
(276) Wenninger, M. J. Model 17: the Snub Cube. *Polyhedron Models*; Cambridge University Press: Cambridge, **1989**; p 31.
(277) Wenninger, M. J. Model 15: Rhombitruncated Octahedron. *Polyhedron Models*; Cambridge University Press: Cambridge, **1989**; p 29.
(278) Etter, M. C.; Reutzel, S. M. *J. Am. Chem. Soc.* **1991**, *113*, 2586–2598.
(279) Etter, M. C.; Baures, P. W. *J. Am. Chem. Soc.* **1988**, *110*, 639–640.
(280) Duchamp, D. J.; Marsh, R. E. *Acta Crystallogr.* **1969**, *B25*, 5–19.
(281) Herbstein, F. H.; Kapon, M.; Reisner, G. M. *J. Inclusion Phenom.* **1987**, *5*, 211–214.
(282) Herbstein, F. H. *Top. Curr. Chem.* **1987**, *140*, 107–139.
(283) Sharma, C. V. K.; Zaworotko, M. J. *Chem. Commun.* **1996**, 2655–2656.
(284) Lough, A. J.; Wheatley, P. S.; Ferguson, G.; Glidewell, C. *Acta Crystallogr.* **2000**, *56*, 261–272.
(285) Ferguson, G.; Glidewell, C.; Mcmanus, G. D.; Meehan, P. R. *Acta Crystallogr.* **1998**, *54*, 418–421.
(286) Ranganathan, A.; Pedireddi, V. R.; Sanjayan, G.; Ganesh, K. N.; Rao, C. N. R. *J. Mol. Struct.* **2000**, *522*, 87–94.
(287) Anastas, P. T.; Williamson, T. C. *ACS Symp. Ser.* **1996**, *626*, 1–17.
(288) Goldberg, I. *Chem. Eur. J.* **2000**, *6*, 3863–3870.
(289) Hagrman, D.; Hagrman, P. J.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3165–3168.
(290) Biradha, K.; Dennis, D.; MacKinnon, V. A.; Sharma, C. V. K.; Zaworotko, M. J. *J. Am. Chem. Soc.* **1998**, *120*, 11894–11903.
(291) Sharma, C. V. K.; Bauer, C. B.; Rogers, R. D.; Zaworotko, M. J. *Chem. Commun.* **1997**, 1559–1560.
(292) Melendez, R. E.; Zaworotko, M. J. *Supramol. Chem.* **1997**, *8*, 157–168.
(293) Plaut, D. J.; Lund, K. M.; Ward, M. D. *Chem. Commun.* **2000**, 769–770.
(294) Biradha, K.; Zaworotko, M. J. *Cryst. Eng.* **1998**, *1*, 67–78.
(295) Russell, V. A.; Ward, M. D. *New J. Chem.* **1998**, *22*, 149–153.
(296) Russell, V. A.; Ward, M. D. *J. Mater. Chem.* **1997**, *7*, 1123–1133.
(297) Russell, V. A.; Evans, C. C.; Li, W. J.; Ward, M. D. *Science* **1997**, *276*, 575–579.
(298) Russell, V. A.; Etter, M. C.; Ward, M. D. *Chem. Mater.* **1994**, *6*, 1206–1217.
(299) Russell, V. A.; Etter, M. C.; Ward, M. D. *J. Am. Chem. Soc.* **1994**, *116*, 1941–1952.

(300) Swift, J. A.; Russell, V. A.; Ward, M. D. *Adv. Mater.* **1997**, *9*, 1183–1186.

(301) Frostman, L. M.; Ward, M. D. *Langmuir* **1997**, *13*, 330–337.

(302) Russell, V. A.; Ward, M. D. *Acta Crystallogr.* **1996**, *B52*, 209–214.

(303) Boucher, E.; Simard, M.; Wuest, J. D. *J. Org. Chem.* **1995**, *60*, 1408–1412.

(304) Gallant, M.; Viet, M. T. P.; Wuest, J. D. *J. Am. Chem. Soc.* **1991**, *113*, 721–723.

(305) Vaillancourt, L.; Simard, M.; Wuest, J. D. *J. Org. Chem.* **1998**, *63*, 9746–9752.

(306) Brunet, P.; Simard, M.; Wuest, J. D. *J. Am. Chem. Soc.* **1997**, *119*, 2737–2738.

(307) Clerk, M. D.; Zaworotko, M. J. *Chem. Commun.* **1991**, 1607–1608.

(308) Copp, S. B.; Holman, K. T.; Sangster, J. O. S.; Subramanian, S.; Zaworotko, M. J. *Dalton Trans.* **1995**, 2233–2243.

(309) Kaczmarek, F.; Jendrzejczak, A. *Opt. Appl.* **1978**, *8*, 3–7.

(310) Roy, U. N. *Iete J. Res.* **1997**, *43*, 245–249.

(311) Reddy, D. S.; Craig, D. C.; Rae, A. D.; Desiraju, G. R. *Chem. Commun.* **1993**, 1737–1739.

(312) Herbstein, F. H.; Kapon, M.; Reisner, G. M. *Acta Crystallogr.* **1985**, *B41*, 348–354.

(313) Herbstein, F. H.; Kapon, M.; Reisner, G. M. *Proc. R. Soc. London, Ser. A* **1981**, *376*, 301–318.

(314) Power, K. N.; Hennigar, T. L.; Zaworotko, M. J. *Chem. Commun.* **1998**, 595–596.

(315) Fowler, F. W.; Lauher, J. W. *J. Phys. Org. Chem.* **2000**, *13*, 850–857.

(316) Nguyen, T. L.; Scott, A.; Dinkelmeyer, B.; Fowler, F. W.; Lauher, J. W. *New J. Chem.* **1998**, *22*, 129–135.

(317) Coe, S.; Kane, J. J.; Nguyen, T. L.; Toledo, L. M.; Wininger, E.; Fowler, F. W.; Lauher, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 86–93.

(318) Toledo, L. M.; Musa, K. M.; Lauher, J. W.; Fowler, F. W. *Chem. Mater.* **1995**, *7*, 1639–1647.

(319) Toledo, L. M.; Lauher, J. W.; Fowler, F. W. *Chem. Mater.* **1994**, *6*, 1222–1226.

(320) Chang, Y. L.; West, M. A.; Fowler, F. W.; Lauher, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 5991–6000.

(321) Davey, R. J.; Williams-Seton, L.; Lieberman, H. F.; Blagden, N. *Nature* **1999**, *402*, 797–799.

(322) Williams-Seton, L.; Davey, R. J.; Lieberman, H. F. *J. Am. Chem. Soc.* **1999**, *121*, 4563–4567.

(323) Aakeroy, C. B.; Nieuwenhuyzen, M.; Price, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 8986–8993.

(324) Kasai, K.; Aoyagi, M.; Fujita, M. *J. Am. Chem. Soc.* **2000**, *122*, 2140–2141.

(325) Zaworotko, M. J. and Moulton, B. Unpublished results.

(326) Cheng, C. M.; Egbe, M. I.; Grasshoff, J. M.; Guarrera, D. J.; Pai, R. P.; Warner, J. C.; Taylor, L. D. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 2515–2519.

(327) Ranford, J. D.; Vittal, J. J.; Wu, D. Q. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1114–1116.

(328) Hollingsworth, M. D.; Werner-Zwanziger, U.; Brown, M. E.; Chaney, J. D.; Huffman, J. C.; Harris, K. D. M.; Smart, S. P. *J. Am. Chem. Soc.* **1999**, *121*, 9732–9733.

(329) Hollingsworth, M. D.; Brown, M. E.; Hillier, A. C.; Santarsiero, B. D.; Chaney, J. D. *Science* **1996**, *273*, 1355–1359.

(330) Brown, M. E.; Chaney, J. D.; Santarsiero, B. D.; Hollingsworth, M. D. *Chem. Mater.* **1996**, *8*, 1588–1591.

(331) Hollingsworth, M. D. *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 514–521.

(332) Brown, M. E.; Hollingsworth, M. D. *Nature* **1995**, *376*, 323–327.

(333) Hulliger, J.; Roth, S. W.; Quintel, A.; Bebie, H. *J. Solid State Chem.* **2000**, *152*, 49–56.

(334) Langley, P. J.; Hulliger, J. *Chem. Soc. Rev.* **1999**, *28*, 279–291.

(335) Hulliger, J.; Langley, P. J.; Roth, S. W. *Cryst. Eng.* **1998**, *1*, 177–189.

(336) Roth, S. W.; Langley, P. J.; Quintel, A.; Wubbenhorst, M.; Rechsteiner, P.; Rogin, P.; Konig, O.; Hulliger, J. *Adv. Mater.* **1998**, *10*, 1543–1546.

(337) Konig, O.; Burgi, H. B.; Armbruster, T.; Hulliger, J.; Weber, T. *J. Am. Chem. Soc.* **1997**, *119*, 10632–10640.

(338) Hulliger, J.; Rogin, P.; Quintel, A.; Rechsteiner, P.; Konig, O.; Wubbenhorst, M. *Adv. Mater.* **1997**, *9*, 677–680.

(339) Hoss, R.; Konig, O.; Kramerhoss, V.; Berger, U.; Rogin, P.; Hulliger, J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1664–1666.

(340) Hulliger, J.; Konig, O.; Hoss, R. *Adv. Mater.* **1995**, *7*, 719–721.

(341) Sra, A. K.; Andruh, M.; Kahn, O.; Golhen, S.; Ouahab, L.; Yakhmi, J. V. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2606–2609.

(342) Pan, L.; Huang, X. Y.; Li, J. *J. Solid State Chem.* **2000**, *152*, 236–246.

(343) Yuen, T.; Lin, C. L.; Mihalisin, T. W.; Lawandy, M. A.; Li, J. *J. Appl. Phys.* **2000**, *87*, 6001–6003.

(344) Li, J.; Chen, Z.; Wang, R. J.; Proserpio, D. M. *Coord. Chem. Rev.* **1999**, *192*, 707–735.

(345) Chen, Z.; Wang, R. J.; Li, J. *Chem. Mater.* **2000**, *12*, 762–766.

(346) Lawandy, M. A.; Huang, X. Y.; Wang, R. J.; Li, J.; Lu, J. Y.; Yuen, T.; Lin, C. L. *Inorg. Chem.* **1999**, *38*, 5410–5414.

(347) Lu, J. Y.; Cabrera, B. R.; Wang, R. J.; Li, J. *Inorg. Chem.* **1999**, *38*, 4608–4611.

(348) Schmitz, M.; Leininger, S.; Fan, J.; Arif, A. M.; Stang, P. J. *Organometallics* **1999**, *18*, 4817–4824.

(349) Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2639–2684.

(350) Zapf, P. J.; Haushalter, R. C.; Zubieta, J. *Chem. Commun.* **1997**, 321–322.

(351) Newkome, G. R.; He, E. F.; Moorefield, C. N. *Chem. Rev.* **1999**, *99*, 1689–1746.

(352) von Schnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 33–51.

CR9900432