Crystal Engineering of Diamondoid Networks

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1 Introduction

That it might ultimately become feasible routinely to design and control solid-state architecture and therefore function, coupled with our growing understanding of supramolecular chemistry, has afforded the driving force behind the emergence of crystal engineering.[1,2] A fundamental principle of crystal engineering is that crystal structures can be regarded as *de facto* manifestations of self-assembly. Whereas this is not always a reasonable assertion in the absence of conventional (*i.e.* $X{-}H\cdots Y$; X,Y = O or N) hydrogen or covalent bonds,[3] it is becoming increasingly clear that molecules or ions of dramatically variable chemical nature can have analogous crystal engineering functions. Therefore, the solid-state structures of moieties as different as a carbon atom, a water molecule, and a dihydrogenphosphate anion have similarities since they represent moieties that have similar geometry (T_d or pseudo T_d) and function (ability to self-assemble) at the molecule or ionic level. Indeed, ice and KH_2PO_4 (KDP) represent simple compounds which have long been known[4] to be capable of exhibiting diamondoid architecture in the solid state, well before the term crystal engineering was introduced by Schmidt.[5] Figure 1 schematically illustrates the similarities and differences between the structures of diamond, ice, and KDP by comparing adamantoid portions of their networks. Whereas all three structures are adamantoid, increased separations between the tetrahedral centres impart important physical consequences: diamond is well enough packed to be mechanically strong and possess one of the highest melting points known; ice is not as efficiently packed and is therefore less dense than water; KDP is so open an architecture that for an isolated network more than 50% of its volume would be vacuum. It is the latter which represents one of several reasons why a search for new diamondoid compounds is of more than aesthetic relevance:

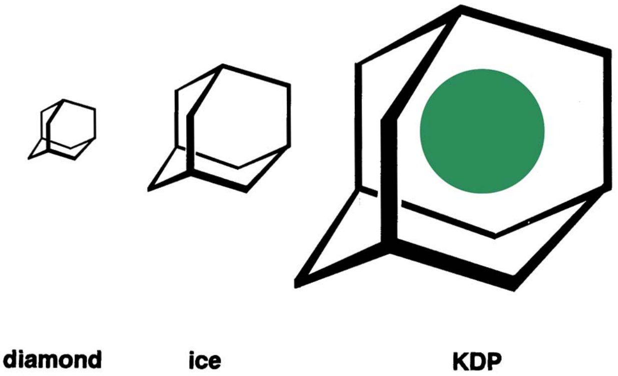


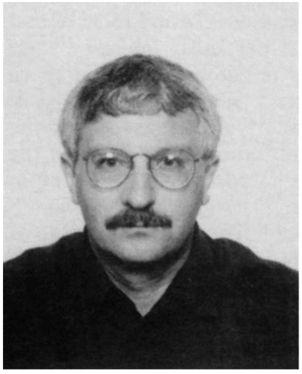
Figure 1 A schematic representation of the adamantoid portion of the diamondoid architectures exhibited by diamond, ice, and KDP. Ice I is a hexagonal network but two polymorphs of ice are diamondoid.

(i) The ability of all 2-D and 3-D frameworks to pack optimally is prejudiced by the directionality and rigidity of the cohesive forces involved. Therefore, diamond is thermodynamically less stable than graphite under ambient conditions and the much larger amount of open space that is necessarily present in a 1-fold diamondoid array of $H_2PO_4^-$ anions has to be accommodated. In the case of KDP, space is addressed by interpenetration of a second independent network, *i.e.* KDP is a 2-fold diamondoid structure. If interpenetration could be reduced, or even avoided, then channels and cavities with very specific and predictable dimensions and chemical type would be generated. Enclathrated guest molecules that facilitate more efficient packing would be expected to promote lower levels of interpenetration and such is indeed the case for trimesic acid (1,3,5-benzenetricarboxylic acid), which is a 3-fold 2-D honeycomb grid when pure.[6] In principle, synthesis of a new generation of open solids with very selective zeolite-like inclusion capabilities is therefore achievable *via* diamondoid architecture.

(ii) Notwithstanding problems associated with packing efficiency, diamondoid solids would in general be expected to have high mechanical and thermal stability because the attractive forces extend isotropically in three dimensions. This includes hydrogen-bonded networks, which can be sustained by hydrogen bond energies of as high as 200 kJ/mol if ionic components are involved.[2]

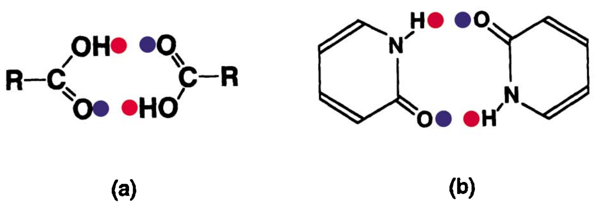
(iii) Even a moiety with perfect T_d symmetry possesses no centre of inversion. It should therefore logically follow that diamondoid architecture is at the very least not predisposed to adapt non-polar space groups. This might seem obvious, or even trivial, but it should be remembered that around 75% of compounds crystallize in non-polar space groups and strategies for designing polarity into crystals are still in their infancy.[7] This is an important consideration since a number of important physical properties (*e.g.* ferroelectricity, piezoelectricity, pyroelectricity, second-order non-linear optics) are dependent upon bulk crystal polarity, which only occurs in compounds that adapt polar space groups. Indeed, a low-temperature polymorph of KDP is a commercial second-order non-linear optic.[8]

Michael J. Zaworotko was born in Blackwood, Gwent and attended Bedwellty Grammer School before graduating from Imperial College in 1977. His Ph.D. was earned with Jerry Atwood at the University of Alabama (X-ray crystallograpy, organoaluminum chemistry, 1982) and this was followed by a postdoctoral fellowship with S. R. Stobart at the University of Victoria, Canada. A research programme dedicated to molecular recognition was initiated when he was appointed Assistant Professor of Chemistry at Saint Mary's University in 1985. The initial focus was ionic liquids but a sabbatical leave at the U.S. Air Force Academy facilitated a change of focus to the solid state, in particular structure–function relationships and crystal engineering in multi-component systems such as organic salts and cocrystals. Dr. Zaworotko is now Associate Professor and Chairperson.



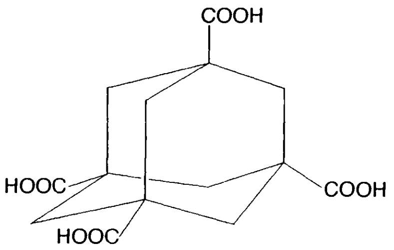
2 The Modular Approach to Crystal Engineering of Diamondoid Networks

The key to successful crystal engineering of new classes of diamondoid compound lies with recognition that, regardless of their chemical nature, molecules, ions or, importantly, combi-



(a) (b)

Figure 2 A schematic representation of the dimeric motifs adapted by (a) carboxylic acids and (b) pyridones. For this and subsequent diagrams the colour coding is red for hydrogen bond donors and blue for hydrogen bond acceptors. Complementarity therefore occurs when blue and red moieties are matched with one another.



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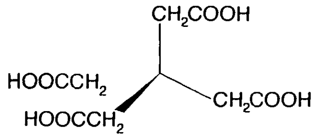

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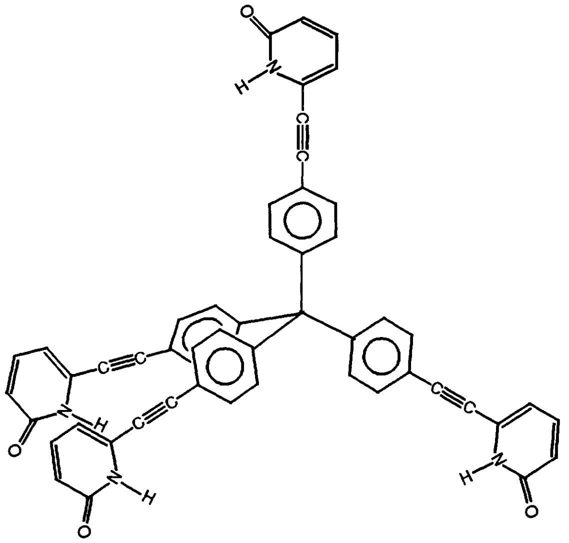


(3)

nations thereof, should be capable of forming infinite diamondoid arrays if their geometry and functionality are appropriate. Whereas the structures of ice and KDP have long been understood, it was not until 1988 that diamondoid frameworks based upon organic molecules were first characterized. Otto Ermer's elegant studies on the tetragonally elongated diamondoid structures of adamantane-1,3,5,7-tetracarboxylic acid^{9a} (1) and methanetetraacetic acid^{9b} (2), detailed not only their crystal structures but provided an excellent introduction to the background and possible future applications of diamondoid solids. It should not be surprising that (1) and (2) are extensively interwoven (5-fold and 3-fold, respectively) since the separations between tetrahedral centres are 10.07 and 8.76 Å, respectively. The observed structures are based upon self-assembly sustained by the carboxylic acid dimer motif. Pyridones exhibit a similar ability to form dimeric motifs (Figure 2) and Wuest exploited this motif with the tetrakispyridone (3) which, remarkably, does not interpenetrate in the presence of butyric acid. Rather, (3) exists as a 1-fold framework with channels large enough to hold two molecules of butyric acid.^{10} Structures (1)—(3) therefore represent molecules that, because of their inherent symmetry and functionality, are effectively programmed to self-assemble to form superdiamondoid arrays.

Unfortunately, tetrafunctionalized molecules with T_d or close to T_d symmetry are not that common. Furthermore, chemical modification of (1)—(3) could easily destroy their ability to self-assemble predictably, and generating new molecules is synthetically challenging. Bearing this in mind, we set out to investigate the possibility of generating diamondoid networks using complementary molecules, *i.e.* a modular or strict self-assembly^{11} approach. In principle, such a strategy has distinct advantages over single-component self-assembly since it could permit fine-tuning of diamondoid structures without resorting to covalent modifications and would therefore be both facile and more generic (Figure 3). Therefore, although significant advances have recently been made with single-component self-assembly^{9,10} and covalent systems such as polychalcogenides,^{12} this review places particular emphasis upon systems which have been prepared *via* the modular approach. Such an approach could involve either non-covalent or covalent bonding and the remainder of this work is subdivided accordingly.

3 Non-covalent Diamondoid Networks

A T_d molecule that is either a tetrafunctional hydrogen bond donor or a tetrafunctional hydrogen bond acceptor that is NOT capable of self-assembling (*i.e.* it does not contain internal complementarity) should in principle strictly self-assemble with two equivalents of a complementary difunctional linear molecule to form a diamondoid array (Figure 3). The T_d molecule we chose to study is $[Mn(CO)_3(\mu_3\text{-}OH)]_4$, (4) an air- and water-stable cubane-like cluster that can be prepared quantitatively from Mn_2CO_{10}.^{13} Structure (4) is illustrated in Figure 4 and it should be clear that it is ideally suited as a prototypal molecule for sustaining diamondoid architecture since it holds perfect T_d symmetry, meaning that all four of its μ_3-OH groups are oriented towards the vertices of a tetrahedron. Furthermore, (4) is rigid and contains no strong hydrogen bond acceptor moieties. Given Etter's observations concerning hydrogen bonding in solids,^{14} that (4) spontaneously self-assembles with 1,2-diaminoethane to form a diamondoid array^{15} should therefore not be a surprise. 1,2-diaminoethane can be replaced with other complementary 'spacers' in a remarkably facile and general manner since the only criteria that matter are that a 'spacer' has two hydrogen bond acceptor moieties and that they can orient their vectors 180° apart from each other. Table 1 lists difunctional molecules that fit these criteria and have been successfully exploited as linear 'spacers'. The 'spacer' molecules employ several classes of hydrogen bond, both conventional (O–H···N, O–H···O) and weak (O–H···arene), and the levels of interpenetration are logical, based upon the length [molecules of (4) are separated by between 9.74 and 15.35 Å] and volume of the spacer molecule. Of particular interest is that every network except one adapts tetragonal or cubic space groups that allow (4) to retain at least S_4 or even T_d symmetry. In other words, the symmetry of (4) clearly manifests itself on the crystal architecture and space group symmetry. Several of the networks are polar or they contain microchannels that contain as many as four molecules of solvent (acetonitrile) per molecule of (4).^{16} Figure 5 illustrates the 4-fold diamondoid structure of $(4)\cdot 2(4,4'\text{-dipyridyl})\cdot 2CH_3CN$ viewed down the tetragonal *c*-axis. The microchannels enclathrate two molecules of acetonitrile per molecule of (4). Several of the structures are diamondoid because μ_3-OH moieties form π-hydrogen bonds with each face of a range of arenes, including napthalenes. The π-hydrogen bonds can be assumed to be quite weak from a thermodynamic

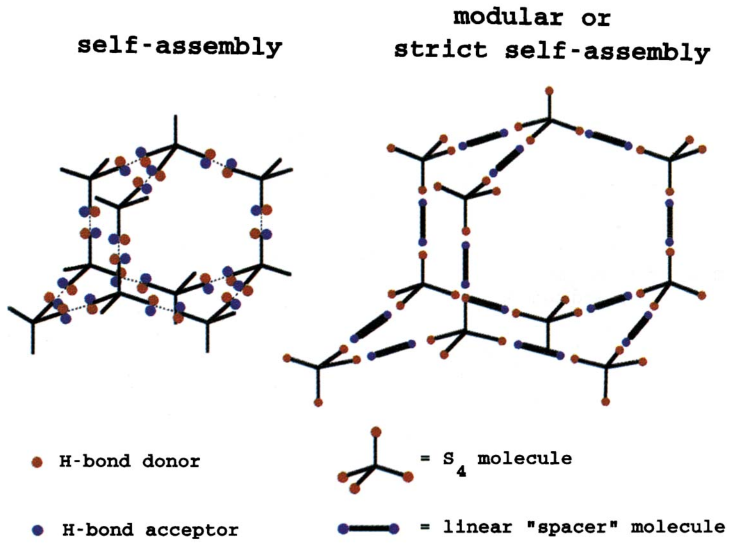
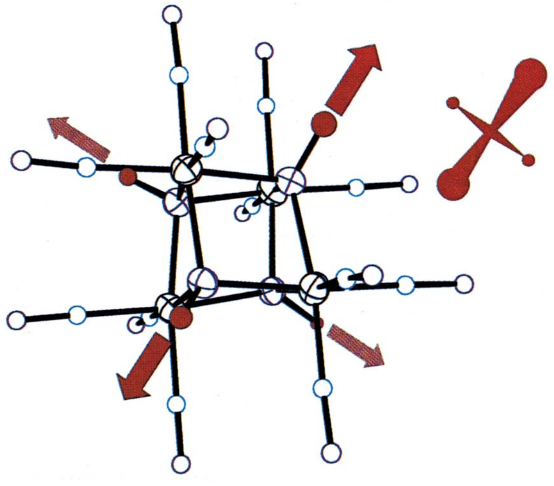


Figure 3 A schematic representation of single-component (self-assembly) *versus* multi-component (strict self-assembly) approaches to construction of diamondoid architectures. The modular nature of the latter makes it in principle facile to 'fine-tune' the bulk physical properties of the network by substituting components that have the same crystal engineering function of either the spacer or the S_4 molecule.



(4)

Figure 4 The molecular structure of $[Mn(CO)_3(\mu_3\text{-}OH)]_4$, (4). Note that (4) has four strong hydrogen bond donors (red) but no strong hydrogen bond acceptors.

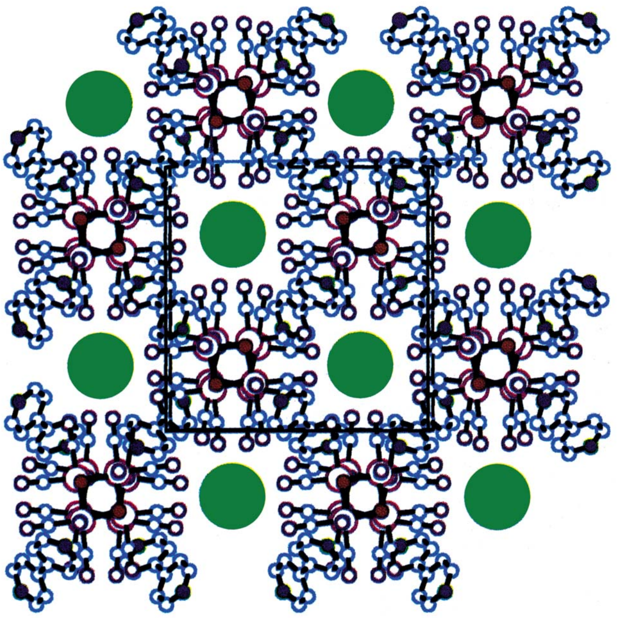


Figure 5 The 4-fold diamondoid structure of (4)•2(4,4′-dipyridyl) viewed down the crystallographic *c*-axis. The microchannels (green circles) are occupied by two molecules of acetonitrile per molecule of (4).

perspective[17] but they are directional and hence capable of acting as linear 'spacers' to sustain the diamondoid architecture. An adamantoid portion of (4)•2*p*-xylene is illustrated in Figure 6. This plot is effectively generic for the (4)•2arene structures since all six we have thus far prepared and characterized exhibit 2-fold interpenetration because of similar intercube spacings.

It is important to recognize that the solvent used for recrystallization can play a critical role in the self-assembly process and even determine the topology of the resulting network. The compounds in Table 1 were crystallized from acetonitrile or the pure 'spacer' molecule. However, if an alcohol is used it can play a crystal engineering function by using its OH group as a donor–acceptor moiety. Therefore, although (4)•2(4,4′-dipyridyl)•2ROH has the same stoichiometry as its acetonitrile analogue, it exhibits a radically different structure based upon interwoven 2-D square grids.[18] The alcohol molecules serve the function of angular 'spacers' that link one end of molecules of

Table 1 Diamondoid networks based upon $[M(CO)_3(\mu_3\text{-}OH)]_4$ and A–A spacers

M	A–A	Intercube Å	Crystal System	*n*-fold
Mn	$Me_2NCH_2CH_2NMe_2$	11.35	Tetragonal	2
Mn	$H_2NCH_2CH_2NH_2$	11.59	Cubic	3
Re	1,4-Diaminobenzene	11.79	Tetragonal	2*
Mn	2-Cl-Pyrazine	11.82	Cubic	3
Mn	$Ph_2P(O)CH_2CH_2P(O)Ph_2$	13.53	Tetragonal	2*
Mn	4,4′-Dipyridyl	15.22	Tetragonal	4*
Mn	4,4′-Bipiperidine	15.35	Tetragonal	4*
Mn	Toluene	10.10	Tetragonal	2,*B*1
Mn	*p*-Xylene	10.35	Tetragonal	2,*B*1
Mn	*p*-Fluorotoluene	10.13	Tetragonal	2,*B*1
Mn	Benzene	9.74	Cubic	2,*A*
Mn	Naphthalene	10.40	Tetragonal	2,*B*2
Mn	Me-naphthalene	10.26	Hexagonal	2,*B*2

* Solvent enclathrated in microchannels. *A*: symmetric bridge; *B*1: unsymmetric bridge to same ring; *B*2: unsymmetric bridge to different rings.

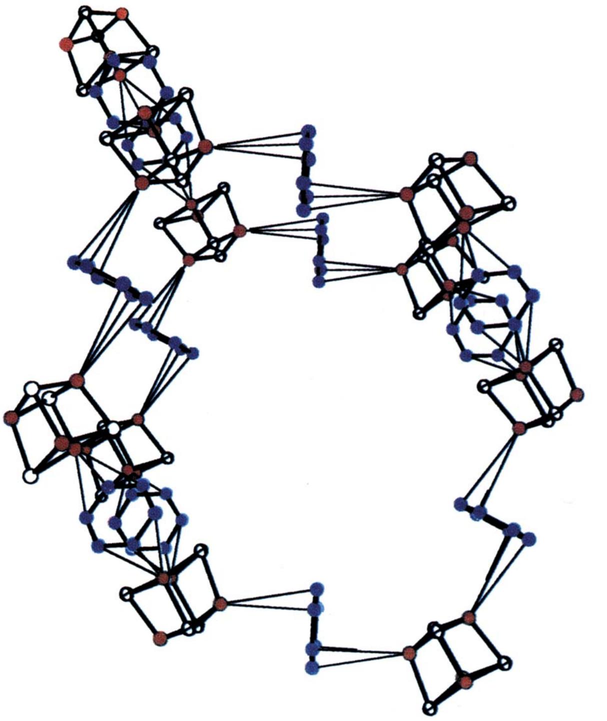


Figure 6 An ORTEP view of the adamantoid portion of one of the two diamondoid networks present in (4)•2(*p*-xylene). Methyl and carbonyl groups are omitted for the sake of clarity.

4,4′-dipyridyl to molecules of (4), thereby preventing propagation in the third dimension required for diamondoid architecture. (4)•2(4,4′-dipyridyl)•2ROH therefore represents strict self-assembly of three complementary molecules in a predictable manner. Difunctional hydrogen bond acceptor molecules that are angular in their own right (1,3-diaminopropane)[18] or linear difunctional acceptors that can form acute hydrogen bonds [1,2-bis(4-dipyridyl)ethane, 1,4-dicyanobenzene] afford co-crystals of the same stoichiometry which exhibit 2-D square grid instead of diamondoid topology. Figure 7 illustrates schematically how T_d molecules can play a modular role in construction of 2-D square grid frameworks.

4 Covalent Diamondoid Networks

There is virtually no limit to where one could begin in terms of designing covalent diamondoid networks since any tetrahedral moiety is in principle capable of sustaining diamondoid architecture and they are known to exist for most elements. Indeed, M_4X_4 analogues of (4) are known for many transition and main group elements. However, in terms of synthetic accessibility, tetrahedral transition metal cations offer a particularly tempting target for the following reasons: their simple coordination chemistry is generally well documented; geometry and lability can be readily controlled using redox; it would be conceivable to incorporate metal centres that are catalytically active. Tetrahedral metal centres would therefore serve the same crystal engineering function as the T_d donor molecule in Figure 3 and metal–ligand bonds would replace hydrogen bonds. It is not necessary to develop new synthetic methodology, rather one has simply to focus upon bridging (*i.e.* exodentate) rather than chelating (*i.e.* endodentate) ligands. General strategies for modular construction of infinite coordinate covalent frameworks were delineated by Robson and Hoskins in 1990[19] and in the past five years there have been several notable examples of diamondoid frameworks based upon Cu^I, Zn^{II}, Cd^{II}, and Ag^I that were rationally constructed: $Zn(CN)_2$ and $Cd(CN)_2$:$Zn(CN)_2$ and $Cd(CN)_2$ exist as isostructural 2-fold diamondoid networks and have been extensively investigated by at least two groups.[19,20] $Cd(CN)_2$ represents a simple and straightforward example of the modular approach described in Figure 3 and shows a rich array of chemistry because it can undergo a honeycomb–diamondoid topological rearrangement within a single crystal[21] and it can act as a host matrix when 1-fold or hexagonal.[20,22]

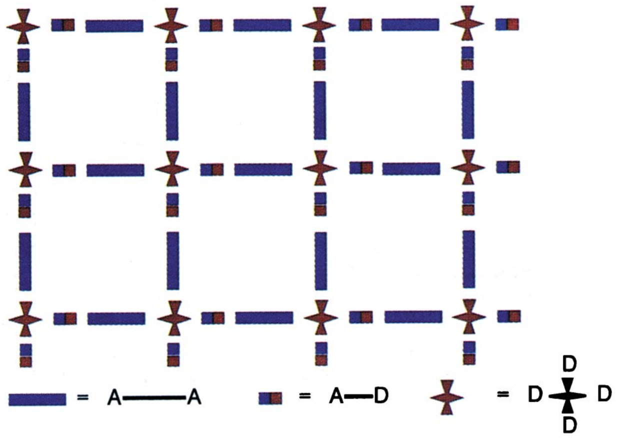


Figure 7 A schematic representation of how three types of molecule with the appropriate symmetry and functionality (1 × T_d donor, 2 × linear difunctional acceptor, 2 × angular donor–acceptor) can strictly self-assemble to form a square grid network.

$Cd(SPh)_2$:$Cd(SPh)_2$ exists in the solid state as a 3-D array of phenylsulfide-linked $Cd_4(SPh)_6^{2+}$ adamantoid cages[23] as illustrated in Figure 8. $Cd(SPh)_2$ therefore represents an unusual example of a covalently linked T_d metal cluster. The authors suggested that $Cd(SPh)_2$ might exist as a higher-order tetraadamantoid cluster $Cd_{10}(SPh)_{20}$ in dimethylformamide, which represents yet another candidate for generating diamondoid architecture. Indeed, cubane-like and adamantoid clusters are known for a variety of metals but are yet to be exploited in a crystal engineering context. The possibility of cooperativity within and between linked clusters provides added impetus for further study in this area.

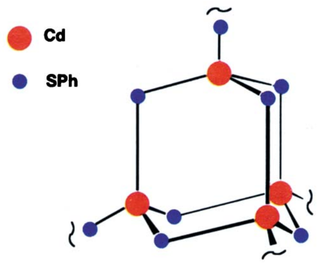


Figure 8 A schematic representation of the adamantoid units that exist in $Cd(SPh)_2$.

$[CuL_2]^+$:Cu^I commonly adapts a tetrahedral environment and as such sustains 5-fold, 4-fold, and 1-fold cationic diamondoid frameworks with 1,4-dicyanobenzene (BF_4^- salt),[22b] 4,4′-dipyridyl (PF_6^- salt[24]) and 2,5-Me_2pyrazine (PF_6^- salt[25]), respectively. Anions sit in microchannels and do not interact with the Cu^I moieties. Remarkably, the structure of the $[Cu(4,4'\text{-dipyridyl})_2]PF_6$ salt closely resembles that of (4)•2(4,4′-dipyridyl)•$2CH_3CN$. Both compounds utilize 4,4′-dipyridyl as a 'spacer' molecule and crystallize as 4-fold diamondoid structures (Figure 9) that contain microchannels parallel to the crystallographic *c*-axis of tetragonal space groups (*P*4/*n* and *P*4/*nnc*, respectively). The former compound holds counterions in its microchannels whereas the latter contains acetonitrile (Figure 5).

Ag^+:$[Ag_2(succinate)]$ dimerizes in the solid state to form linked planar tetranuclear $[Ag_4(succinate)_2]$ clusters that have S_4 symmetry because of the disposition of the succinate moieties (Figure 10). The clusters are bridged to one another by succinate dianions, thereby forming a 3-fold diamondoid solid.[26] This is

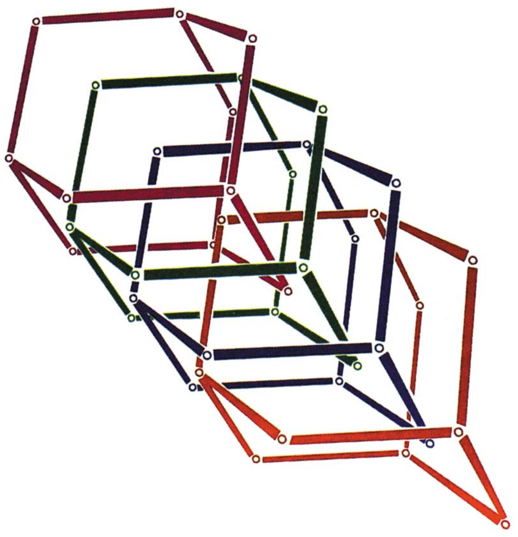


Figure 9 A schematic representation of how four adamantoid units can interweave.

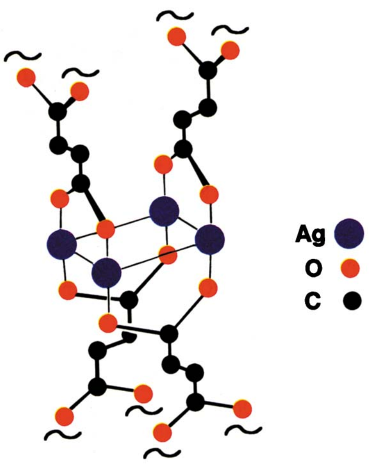


Figure 10 A schematic representation of the S_4 cluster formed by [Ag_2(succinate)].

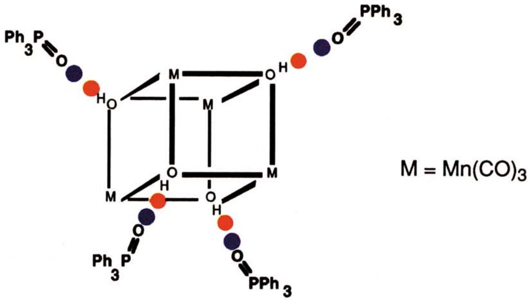
another example of a cluster that links to form diamondoid networks and illustrates an important concept: overt S_4 symmetry is not necessary to form diamondoid arrays.

5 Summary and Future Directions

The focus of this review has been upon how modular approaches can be successfully applied to designing one particular type of structure: diamondoid solids. What do these results mean in a wider context? The author considers that the results are important not so much because of what was achieved but how it was achieved. The results presented herein demonstrate not only that the modular approach to crystal engineering of diamondoid networks is viable, but that it can be applied across a diverse range of chemical components (from organics to metal clusters) and bonds (π-hydrogen bond to coordinate covalent). Therefore, given that it is now possible rationally to exploit the directionality of both non-covalent and covalent bonds in order to crystal-engineer diamondoid solids, it is reasonable to assert that the same principles should be equally applicable to other structural classes. When such observations are coupled with recent advances in cognate fields such as computational, host–guest chemistry and materials characterization, scientists are finally in position to have gathered enough tools to understand and control solid-state structure–function relationships well enough to aim realistically at equalling or surpassing the functions of naturally occurring materials. The author is optimistic enough to believe that crystal engineering will evolve to the point where the only limits that the chemist will face in the context of designing new functional materials is his or her imagination. Minerals might therefore merely serve as prototypes for new classes of 'fine-tunable' mineralomimetic solid that can be crystal-engineered, for example, to have zeolitic, catalytic, specific bulk physical properties, or a combination thereof. Indeed, this is the ultimate goal of crystal engineering: control of solid-state structure to the extent that specific function can be routinely and rationally incorporated. Such optimism might have been very difficult to justify as recently as 1988 when Maddox made the following provocative statement '*One of the continuing scandals in the physical sciences is that it remains in general impossible to predict the structure of even the simplest crystalline solids from a knowledge of their chemical composition*'.[27] Whereas Maddox's statement was qualified by the remainder of his essay it still holds true for the majority of compounds. Indeed, such is the case for (4) when it is pure. However, as should be clear from this review, judicious choice of modular components can validate *ab initio* prediction of at least the gross features of crystal structures and in some cases significantly limit space group choice. Such is the case for several of the compounds listed in Table 1. Indeed, in cases where the 'spacer' moiety and its interaction with (4) is symmetrical enough to facilitate full retention of T_d symmetry [*i.e.* (4) sits around a crystallographic-43*m* position] the space group choices are limited to just six out of two hundred and thirty: *Fd*-3*m* (*cf.* diamond), *Pn*-3*m*, *I*-43*m*, *F*-43*m*, *Fm*-3*m*, or *P*-43*m*. (4)·2 benzene fits the necessary criteria because benzene holds 3-fold symmetry. Measurement of the cell volume of (4)·2benzene dictates that $Z = 2$ and therefore means that *Pn*-3*m* is the only possible space group. The precise structure, including its 2-fold nature, can therefore be determined even before crystallographic data are collected because the positions of molecules of (4) and benzene are fixed by space group symmetry. The lower crystallographic site symmetry of the other compounds in Table 1 is a reflection of the point group of the 'spacer' and the symmetry of its interaction with (4).

Finally, it should be stressed that the lessons that can be gained from crystal engineering would also be expected to be applicable to the design and assembly of discrete supramolecules and nanostructures, and, of course, *vice-versa*. The relationship between crystal engineering and supramolecular chemistry is already documented as are the ideas that, by virtue of their molecular symmetry and functionality, mixtures of molecules can be programmed for a particular structure and function.[28] Indeed, modular or 'molecular meccano'[29] approaches have already been successfully applied to synthesis of a wide range of discrete supramolecular complexes. We have started to investigate (4) in the context of discrete supramolecules since its T_d symmetry and functionality should in principle manifest towards discrete supramolecules if it is mixed with appropriate components. Compound (4) readily forms discrete 4:1 adducts with monofunctional hydrogen bond donors such as triphenylphosphineoxide, (5),[30] whereas in the presence of a crude mixture of dimethyldiazaanthracenes (*i.e.* angular or linear difunctional 'spacers'), the four-component nine-molecule centrosymmetric dimer (6) can be isolated (Figure 11).[31] We had anticipated that (4) would preferrentially recognize only one difunctional 'spacer' of those present in the diazaanthracene 'soup', but instead it sequestered two so as to generate (6). That (4) or any molecule with related symmetry and functionality will have a rich chemistry in the context of discrete supramolecules appears likely if one considers that structural analogies can be drawn between the compounds in Table 1, (5) and (6) and diamond, methane and ethane, respectively.

I would like to acknowledge my co-workers, whose names appear in the list of references, and the following sources of



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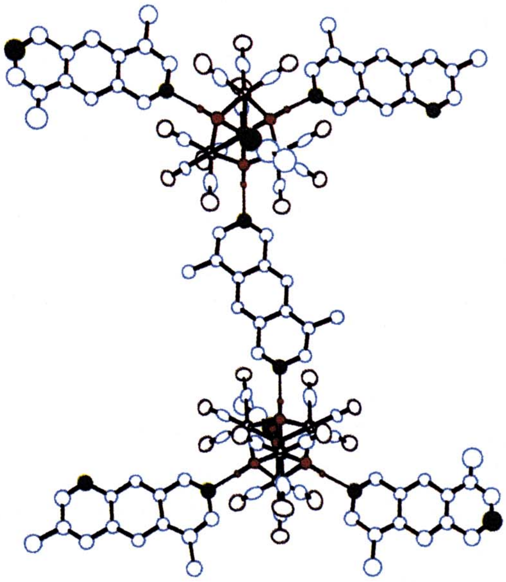

Figure 11 An ORTEP plot of the nine-molecule supramolecular aggregate formed when (4) is crystallized from acetonitrile in the presence of a mixture of dimethyldiazaanthracenes.

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