Inorganic crystal engineering: a personal perspective

Dario Braga

Dipartimento di Chimica G. Ciamician, Università di Bologna, Via F. Selmi 2, 40 126 Bologna, Italy

Received 18th September 2000, Accepted 2nd October 2000

Inorganic crystal engineering is the modelling, synthesis and evaluation of the properties of crystalline materials obtained from inorganic, organometallic and bioinorganic building blocks. This article will take the reader across this interdisciplinary field of research from supramolecular to materials chemistry and biominerals following the collection of papers presented at the Dalton Discussion on Inorganic Crystal Engineering held at the University of Bologna. The focus will not only be on the preparation and characterisation of supermolecules, co-ordination networks, molecular crystals, nanoporous materials and zeolites but also on the investigation of magnetism and conductivity, of Langmuir–Blodgett films, and of nanoporous, amorphous, polymorphic and pseudo-polymorphic systems. Both directions of foreseen development of the inorganic crystal engineering field as well as some of the major drawbacks will be critically discussed.

Introduction

Crystal engineering: a "reborn" discipline

Although the roots of crystal engineering are unquestionably in the organic solid state chemistry field (see below) it is also clear that, at the time of publication of this special issue of *J. Chem. Soc.*, *Dalton Trans.*, the most tumultuous expansion of the discipline is taking place in the directions of inorganic, bioinorganic and co-ordination chemistry.

The qualifier "engineering" associated to crystals was first employed in the late sixties by G. Schmidt and collaborators at the Weizmann Institute to describe the photodimerisation reaction in crystalline cinnamic acid and its derivatives.[1] The idea was relatively simple: topochemical control on photochemical activated cyclisation reactions could occur because the double bonds of the olefins were locked in place by the crystal packing at an appropriate distance for reaction. Schmidt wrote: "The systematic development of our subject will be difficult if not impossible until we understand the intermolecular forces responsible for the stability of the crystalline lattice of organic compounds: a theory of the organic solid state is a requirement for the eventual control of the molecular packing arrangement. Once such a theory exists we shall, in the present context of synthetic and mechanistic photochemistry, be able to 'engineer' crystal structures having intermolecular contact geometries appropriate for chemical reaction, much as, in other contexts, we shall construct organic conductors, catalysts, *etc*." In spite of many scientific efforts, the lack of true predictability of the arrangements that molecules with different shapes could adopt in the solid state inhibited rapid development of the research field.

Almost two decades had to pass before crystal engineering was "reborn". What we today call "crystal engineering" is rather different from what Schmidt had in mind. *Modern* crystal engineering is a hybrid discipline that results from the "mating" of supramolecular chemistry and materials chemistry. Crystal engineering draws its strengths from the synergistic interaction between, on the one hand, design and synthesis of supermolecules and, on the other, design and synthesis of crystalline materials with desired solid state properties. In a way, the definition of supramolecular chemistry put forward by Jean-Marie Lehn in his Nobel lecture[2] "chemistry beyond the molecule bearing on the organised entities of higher complexity that result from the association of two or more chemical species held together by intermolecular forces" seems to encompass crystal engineering. What is a (molecular) crystal if not an "organised entity of higher complexity held together by intermolecular forces"?

The need for a "proactive" approach to crystal design and its potentials in materials chemistry was clearly felt by Margaret Etter.[3] In 1987 she wrote: "Organizing molecules into predictable

Dario Braga

Dario Braga graduated in Chemistry at the University of Bologna in 1977. He was a postdoctoral fellow in Italy and the UK. He joined the Faculty of Science of the University of Bologna in 1982, where he is currently Associate Professor of General and Inorganic Chemistry. He was awarded the Raffaello Nasini Prize from the Inorganic Chemistry Division of the Italian Society of Chemistry in 1988 for his studies on solid state dynamic processes. He received the FEDERCHIMICA Prize for 1995 for his research on intermolecular interactions in organometallic systems. His major current interests are in extramolecular interactions and hydrogen bonding in organometallic materials, and the engineering of organic–organometallic crystals. He is a Member of the Dalton Council, of the international editorial board of Chem. Commun. and of the Research Observatory of Bologna University. He is also the Scientific Editor of Cryst EngComm, the RSC electronic journal devoted to crystal engineering (www.rsc.org/crystengcomm).

DOI: 10.1039/b007602n

arrays is the first step in a systematic approach to designing organic solid-state materials". In 1988, John Maddox, Editor of *Nature*, published an editorial that made a considerable impact: "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 solid from a knowledge of their chemical compositions".[4] This statement has been quoted (when not overquoted) many times to stress how far we all were and are from being able to model the forces responsible for the cohesion of solids. The first book devoted to organic crystal engineering was published in 1990 by Gautam R. Desiraju.[5] Crystal engineering was there defined as: "The understanding of intermolecular interactions in the context of crystal packing and in the utilization of such understanding in the design of new solids with desired physical and chemical properties".

This selection of publication *milestones* is very arbitrary and is meant only to show how, towards the end of the eighties, solid state chemistry (and crystallography) was ready for a cultural "quantum-leap". As a consequence of this circulation of ideas, chemists began to approach crystals differently from what had generally been done till then. Rather than thinking of a crystal as a "molecular container",[6] *i.e.* a box, in which molecules, and ions with identical characteristics and properties could be conveniently packed, synthetic chemists began to think "supramolecularly", *i.e.* with the higher hierarchy of a crystalline arrangement in mind. The need for this new awareness was particularly felt in the inorganic and organometallic fields. With an adequate choice of the structural features of the molecular building blocks, chemists could aim to obtain the desired arrangement and, possibly, the desired supramolecular property. As in supramolecular chemistry, the *collective properties* of the aggregate depend on the choice of intermolecular and inter-ion interactions between components. As in materials chemistry, applications may then be sought in optoelectronics, conductivity, superconductivity, and magnetism as well as in catalysis, molecular sieves, solid state reactivity, and mechanics. It goes without saying that chemists *still* need to synthesise, isolate, and characterise molecules as they have done (and will be doing) for a long time.

Nowadays, crystal engineering may be defined as the modelling, and synthesis of crystalline materials constituted of purposely chosen building blocks joined by supramolecular interactions and the utilisation of programmed chemical and physical properties.[7] This definition is broad and encompasses all types of interactions. As will be apparent from the articles collected in this volume, co-ordination bonds, and/or the convolution of co-ordination bonds with weaker non-covalent interactions such as hydrogen bonds, π–π, Au···Au interactions, with or without the presence of the Madelung field generated by ions, all need to be taken into account when dealing with non-organic systems.[8]

Why inorganic crystal engineering? Properties from architectures

The initial idea, *making crystals with a purpose*, has rapidly grown out of its cradle with strong ramifications in all of the traditional subdivisions of chemistry. Risking to sound paroquial, I daresay that the actual impact of inorganic and co-ordination chemistry is probably the true novelty in the field. Inorganic crystal engineering (ICE) uses transition metal and main group atoms, and hence implies the *whole periodic table of the elements*. A corollary to this expansion is that the roles of charge, dipolar interactions, spin states, orbital levels and all the implications in terms of magnetism, charge transfer, spectroscopy, *etc.* need to be taken into account. While organic crystal engineering (OCE) is mainly concerned with the assembly of molecular crystals *via* non-covalent bonds (mainly van der Waals and hydrogen bonds with little utilisation of ionic charges), inorganic crystal engineering can rely on the utilisation of much stronger interactions, namely co-ordinate bonds and covalent bonds. Hence, materials containing covalent networks or metal-based co-ordination networks are generally much more robust than those based only on organic molecules and on weak interactions between organic building blocks. Clearly, the number of combinations is limited only by the imagination of the researcher but also by what Nature can be induced to accommodate. The abundance of options and the increased robustness of the products is responsible for the rapid increase in ICE and for the decision to hold a Dalton Discussion on this new field of research.

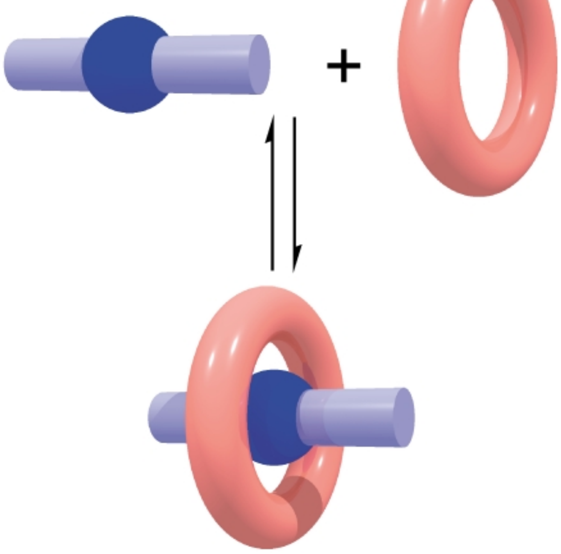


Fig. 1 A schematic representation depicting the formation of a threaded 1:1 complex (a [2]pseudorotaxane) between two complementary species wherein the cavity of a suitably-sized macrocycle is pierced by a linear thread. Reproduced from ref. 9.

The "philosophy" of the Dalton Discussion is summarised in the scheme. This logical path is reflected in the selection of Perspectives and scientific papers quoted through this article.

Supra-molecular Chemistry	Molecular Crystals	Co-ordination Networks	Inorganic Crystal Properties	Crystal Growth and Biomaterials

As pointed out by Stoddart[9] one of the goals of contemporary chemistry is the construction of larger and larger superstructures. The notion of a *molecular meccano kit*, a set of objects and their interlocking to yield thermodynamically stable superstructures, is useful in both supramolecular chemistry and crystal engineering. The concept is schematically illustrated in Fig. 1 where a $R_2NH_2^+$ cation threads through the cavity of a crown ether to form a 1:1 [2]pseudo-rotaxane. In both crystal engineering and supramolecular chemistry the objects (the bits and pieces of the meccano kit) are molecules and ions, while interlocking and assembling (or self-assembling, if we use only one type of object) is attained *via* supramolecular bonding capacity that depends on the functional groups of the building blocks. The resulting properties are collective properties that depend, in the case of crystalline materials, on the convolution of molecular/ionic properties with lattice periodicity. Stoddart has demonstrated that the molecular meccano kit, based on recognition motifs that utilise neutral macrocyclic polyethers to thread onto chains containing benzylic functions and dialkylammonium centres, exploits the formation of hydrogen bonds between the $R_2NH_2^+$ ions and the crown ethers forming *multiply encircled* and *multiply threaded*

Table 1 A non-exhaustive list of network qualifiers and descriptors

Network Qualifiers	Network Descriptors
Diamandoid and adamandoid	Open or interpenetrated
Honeycomb and brick wall	Catenated, self-catenated
Rectangular and square grid	Entangled, self-entangled
Ladder and helix	Knotted, poly-knotted
Bilayer	Interdigitated
α-Po structure	Covalent or non-covalent or ionic
Rutile-type structure	Chiral

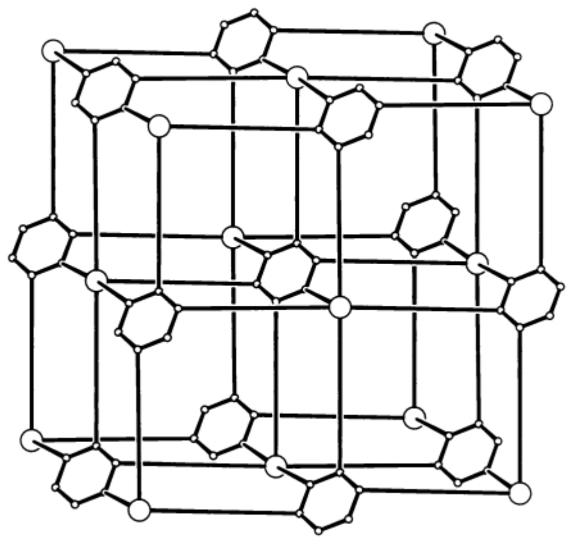


Fig. 2 A network possessing the α-Po structure. Reproduced from ref. 10.

superstructures. We shall see in the following that the *meccano kit* idea is well suited to crystal engineering.

Co-ordination networks

It cannot be denied that co-ordination network engineering takes the "lion's share" of the scientific endeavours in the field of inorganic crystal engineering. Many relevant aspects of co-ordination network engineering are covered by Robson.[10] The strategy underlying the work in this area is summarised by the following phrase from Robson's perspective article: "carefully designed connecting ligands capable of binding metal centres strongly and predictably at chelation sites may afford improved structural control in network assembly". The basic idea is that of utilising the co-ordination bonding capacity of transition metal atoms to build supramolecular arrangements in 3-D obtained by convoluting co-ordination chemistry with crystal periodicity, *i.e.* periodic co-ordination chemistry. It is interesting to note how this branch of chemistry is prolific of new descriptors/adjectives and qualifiers. Table 1 shows a (probably non-exhaustive) compilation of epithets referring to co-ordination network structures taken from the articles published in this issue. Each network descriptor identifies a rather precise structural topology, and the reader will find examples of each type through the articles in this special volume. An example of a co-ordination network possessing the α-Po network is shown in Fig. 2.

It has been observed that many co-ordination network engineering strategies utilise bipyridyl-type ligands (N···N ligands, hereafter) with *at least* two N-donors in suitable geometrical position to act as a bridge between metal atoms such as Ag(I), Cu(I), Ni(II) which form robust N–M dative bonds. This combination ensures not only formation of robust –M–(N···N)–M–(N···N)– networks but also the possibility of varying the topology of the networks by choosing the number of donors and the geometries of the ligands. In such a way, 1-D, 2-D and 3-D superstructures can be obtained. The voids in the superstructures are usually filled either by self-entanglement of the networks (as well discussed by Robson[10]) or by inclusion of solvent or other guest molecules.

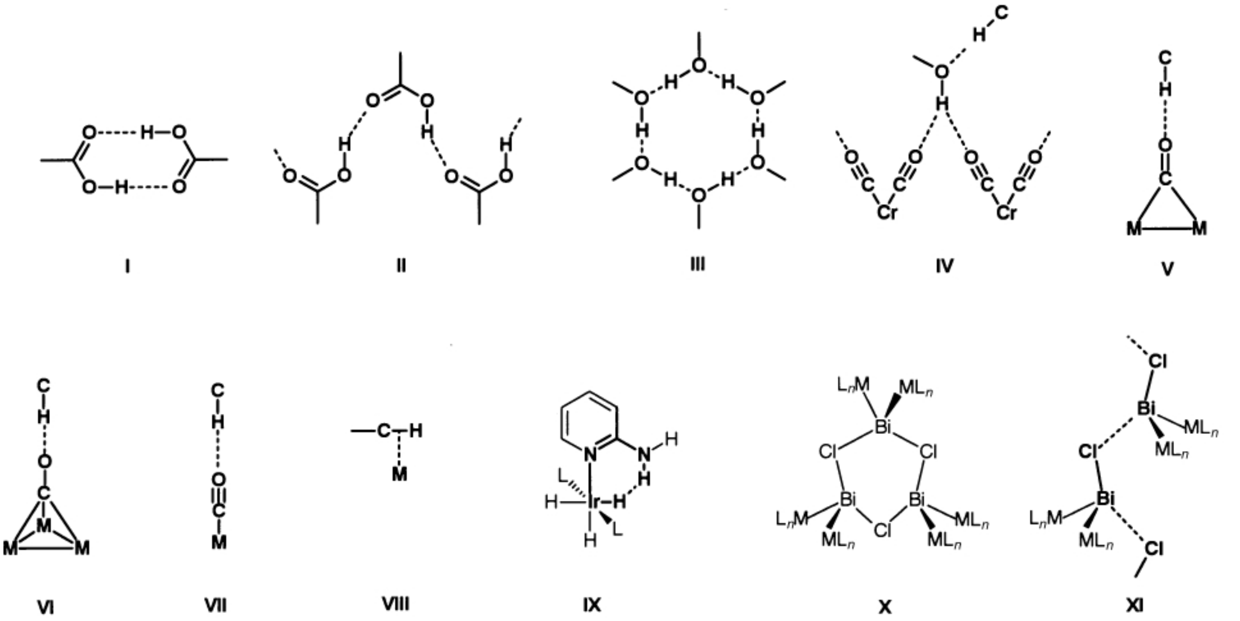
Fujita and Biradha,[11] for example, use bipyridyl-type ligands to link Ni or Cu metal centres to form open and interpenetrated 2-D networks. By varying the length of the ligand the open square grid co-ordination network can be expanded up to a dimension of 15 × 15 Å. It has also been shown that the use of electron deficient guest molecules, such as nitro- and cyano-benzene, allows the preparation of open network square grids with electron rich ligands containing the anthracene moiety.[11] Champness *et al.*[12] use multi-dentate 2,3′-bipyrazine and pyrazino[2,3-*f*]quinoxaline ligands to form Ag(I) co-ordination networks. The role of the counterions and of the solvent has been discussed. Ciani *et al.*[13] use another N···N ligand (2-ethylpyrazine) with Ag(I) to form a co-ordination network containing four-connected metal atoms. In the case of copper the polymeric species $[Cu(bpe)(SO_4)]\cdot 5H_2O$ (bpe = 1,2-bis-(4-pyridyl)ethane) is formed. Removal of the solvent trapped in the interpenetrated network has been investigated by means of thermogravimetric experiments (TGA) while a comparison of the hydrated and anhydrous structures has been carried out by X-ray powder diffraction.

Batten *et al.*[14] use similar bipy-type N···N ligands together with the N-donor dicyanamide $N(CN)_2^-$ ligand and Cu(I) to form diamandoid-like interwoven networks. Zaworotko *et al.*[15] investigate the presence of guest molecules in the nanoporous systems obtained by using simultaneously bipyridine ligands and arenes such as chlorobenzene, dichlorobenzene, benzene, nitrobenzene, toluene and anisole in reactions with $Ni(NO_3)_2$ and $Co(NO_3)_2$ salts. The convolution of the co-ordination network with the molecular network formed by the arenes has been discussed. It has been pointed out that the complementarity between the covalent and non-covalent topology may be exploited to control the overall crystal packing. Evans and Lin[16] report on the utilisation of Cd(II) metal centres to form co-ordination networks based on *meta*-pyridinecarboxylate bridging ligands.

In summary, most of the work on co-ordination networks is focused on the utilisation of organic linkers between metal centres, as pointed out by Robson.[10] The most popular ligands are bidentate N···N bipyridyl-type ligands because of their well known capacity for binding late transition metals strongly, leading to robust superstructures. The bidentate or polydentate ligands exert the function of spacers and linkers between metal centres. They also represent, topologically, the joints and knots holding together the networks. Similar reasoning applies to organometallic crystal engineering where the building blocks are constituted of organic fragments linked *via* direct M–C bonds to one or more metal centres. The phenomena of *self-entanglement* and *interpenetration* represent the major obstacles to the preparation of crystalline materials with large and accessible empty space such as would make them suitable for solid state reactivity, catalysis, utilisation as solid state sensors, *etc.* Some degree of success in the exploitation of this type of artificial nanoporosity has been attained when the crystal structure nucleates and grows together with "removable" guest molecules (see below).

Co-ordination chemistry and hydrogen bonds

Desiraju[17] points out that ICE must pass, as OCE did long before, through the stage of analysis before crystal synthesis can be attempted. The most readily accessible "analytical tool" for the crystal engineering practitioner is represented by the huge depository of structural data available in the Cambridge Structural Database (CSD) and in the Inorganic Crystal Structure Database (ICSD).[19] Indeed, "data-mining" has been of paramount importance for the definition of crystal-oriented



Scheme 1 Structures and supramolecular synthons. Reproduced from ref. 17.

synthetic strategies because it has permitted the discovery of *trends* in crystal packing and the identification of *supramolecular synthons* that can be *used* to construct predefined architectures. Scheme 1 shows some of the synthons that are often encountered in crystals of co-ordination complexes.

One can see that inorganic crystal engineering can benefit from the possibility of combining metal–ligand co-ordination bonding with other, usually weaker, non-covalent bonds. This is clearly not possible in "organic-only" crystal engineering. Although the preference of experimentalists is directed towards hydrogen bonding, because these interactions combine directionality with (relative) strength, π–π interactions have also been shown to play an important role in controlling molecular aggregation. Hydrogen bonds between organometallic species as well as Au · · · Au interactions are discussed in Desiraju's Perspective article.[17] He shows how strong hydrogen bond donor/acceptor groups, such as –COOH and –OH systems, as well as primary $-CONH_2$ and secondary –CONHR amido groups, form essentially the same type of hydrogen bonding interactions whether as part of organic molecules or as metal co-ordinated ligands. This is not surprising, since hydrogen bonds formed by such strong donor and acceptor groups are at least one order of magnitude stronger than are most non-covalent interactions, and are most often already present in solution. In addition to these strong bonds, and to the plethora of weaker (*e.g.* C–H · · · O, C–H · · · N, C–H · · · π *etc.*) 'organic'-type hydrogen bonding interactions, the presence of metal atoms in molecular building blocks generates *new* types of interactions which are characteristic of inorganic and organometallic systems. This subject has also been recently reviewed.[18]

Several research groups are exploiting hydrogen bonded synthons to *combine* co-ordination chemistry and hydrogen bonding. The idea is essentially that of linking (generally *via* an N-terminus or *via* a π-interaction) a ligand carrying a hydrogen bond donor–acceptor system to a metal centre [Pt, Ni, Cu, Ag, *etc.*]. The interplay between the two types of interactions is then responsible for the topology of the resulting supramolecular arrangement. This type of strategy is, for instance, developed by Tasker *et al.*[20] with ditopic ligands based on tetradentate salicylaldimine ligands carrying morpholine substituents capable of trapping sulfate anions, and by Mingos *et al.*[21] with orotate complexes and aminopyridine co-ligands and Pt(II) phosphines. Burrows *et al.*[22] study the co-ordination of thiourea with a series of anions derived from polycarboxylic acids in the formation of Zn-complexes, and investigate the resulting nanoporous structures, which are able to encapsulate water in the channels. In all these cases a prominent packing role is played by interactions of the N–H · · · O type. Brammer *et al.*[23] utilise Cr-co-ordinated arene ligands and N-ligands bound to Pt metals, to construct interesting hydrogen bonded networks. Brammer also notes the role of weaker types of interactions such as C–H · · · π and C–H · · · O. Aakeröy *et al.*[24] use pyridine-based ligands to link together preformed one-dimensional inorganic networks of Cu(I) halides. The hydrogen bonds formed between the organic moieties permit a fair degree of confidence in predicting the way the linear and ladder-type Cu-networks will be joined together. With a related approach Hubberstey *et al.*[25] use tetradentate bis(amidino-*O*-alkylurea) ligands and Cu(II) to investigate the hydrogen bond mediated anion recognition capacity of the complexes towards chloride and ethyl sulfate anions.

The work presented by Orpen *et al.*[26] is based on the utilisation of M–X · · · H–N hydrogen bond synthons to prepare crystalline salts *via* charge-assisted hydrogen bonding interactions between hydrogenated bipyridine ligands (4,4′-H_2bipy) and metal halide anions such as $PtCl_4^{2-}$, $ZnCl_4^{2-}$, $PbCl_4^{2-}$, *etc.* The interactions of the N–H · · · X type are not, *per se*, amongst those regarded as strong hydrogen bonds, but the presence of a positive ionic charge on the donor and of an anionic charge on the accepting co-ordination complex, *e.g.* $N–H^+ \cdots X^-$, reinforces the bond and enhances the directionality of the interaction. In this context, the results reported by Grepioni *et al.*[27] (see also below) provide several other examples of crystalline materials "held together" by charge-assisted hydrogen bonding interactions and coulombic forces between organometallic building blocks such as the dicarboxylic acids $Fe(C_5H_4COOH)_2$ and $[Co(C_5H_4COOH)_2]^+$.

Intermolecular interactions (other than the hydrogen bond)

The role of non-covalent interactions other than hydrogen bonding as complementary tools in crystal engineering is stressed by Desiraju.[17] He envisages, among the interactions that are distinctive of organometallic and co-ordination compounds, the agostic interactions with electron deficient metals (usually early transition metals, such as Zr). It has been argued, however, that these interactions might be too feeble to play any significant role at the supramolecular level. Strength and directionality are, in fact, prerequisites for a given intermolecular interaction to be useful in a design strategy. Even though the interaction that best matches these requirements is unquestionably the hydrogen bond, several papers point to the importance in crystal engineering applications of other interactions which possess a sufficient degree of directionality. For example, graphitic-like π-stacking of metal-bound arene ligands is a recurrent motif in crystalline environments; the paper by Janiak[28] discusses this aspect critically and analyses it statistically, by means of CSD searches, the importance of π···π interactions between N-containing arenes. The competition between π···π and C–H···π interactions has also been discussed.

Other relatively strong interactions are formed by closed-shell atoms,[29] with energies of the order of 10–40 kJ mol^{-1}, *i.e.* weaker than covalent bonds but stronger than most van der Waals interactions. In particular the role of Au···Au interactions has been illustrated by Schmidbaur *et al.*[30] In this work, the Au···Au interactions observed in crystalline $(Me_3P)AuNO_3$ have been compared with other aureophilic interactions present in other $(Me_3P)AuX$ systems, showing that the formation of multi-co-ordination with longer Au···Au contacts or dimerisation with usually shorter Au···Au distances depends on the size and electronegativity of the anions X^-.

The strategy employed by Hosseini *et al.*[31] provides a very good demonstration that van der Waals interactions can also be exploited successfully to construct networks in the solid state based on the utilisation of unsymmetrical bis-calixarene molecules (*koilands*, see below). The combination of koilands with adequate connectors (see Fig. 3) allows the construction of 1-D networks formed by linear arrays of molecules which owe their stability essentially to the key-in-the-lock van der Waals interactions between koilands and connectors.

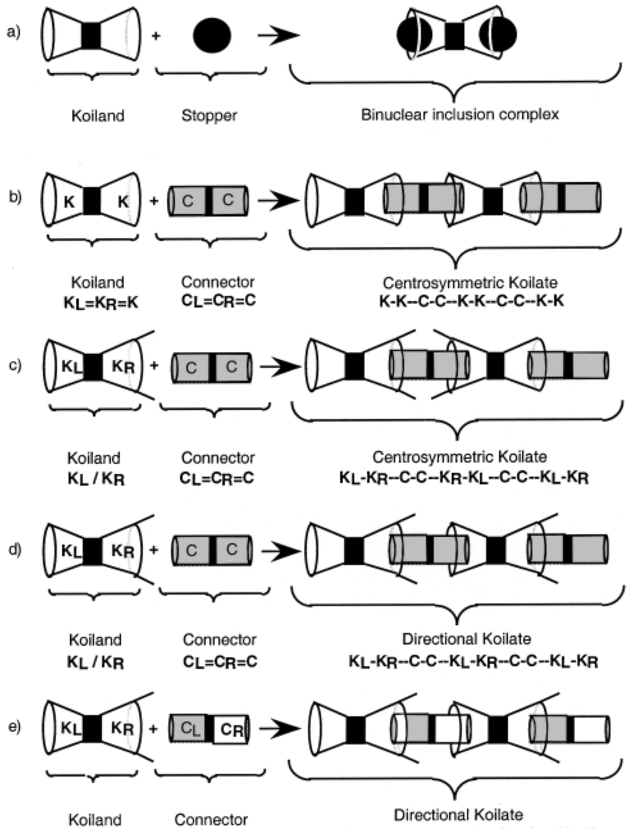


Fig. 3 Schematic representation of discrete binuclear inclusion complexes which may be formed between koilands and stopper molecules (a) and of koilates (1-D inclusion networks) which may be obtained in the presence of connector molecules. The 1-D networks may be non-directional (b, c) or directional (d, e). Reproduced from ref. 31.

Some properties of "crystal engineered" inorganic materials

As mentioned above, nanoporosity, *i.e.* the presence of channels and cavities in network structures constructed according to crystal engineering strategies, is an intriguing phenomenon related to the inclusion of solvent or other guest molecules in the crystal architecture. The inclusion of solvent is often an unpredictable event of a crystallisation process. It is usually regarded as one of the shortcomings of a carefully conceived crystal engineering strategy since *undesired* solvent molecules in the crystals may interfere with the desired set of intermolecular interactions by providing alternative networks of lower energy (and higher entropy). Nanoporosity recalls the behaviour of natural and synthetic zeolites towards guest molecules. The cavities in zeolites interact with guest molecules *via* non-covalent interactions exactly as solvent or other guest molecules interact with the open-framework superstructures observed in some co-ordination networks and hydrogen bonded solids.

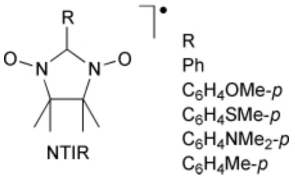
Zecchina *et al.*[32] discuss the interaction between ammonium cations and the structure of defective silicalite containing internal Si–OH nests generated by Si vacancies. It is shown that interactions within silicalite are mainly based on hydrogen bonds of the O–H···O and O–H···N types involving hydroxyl groups. The zeolite was studied by a combination of techniques, including neutron diffraction, IR spectroscopy, and microcalorimetry.

Nanoporosity can also be *turned to advantage*. Papers in this issue show not only that crystal engineers are learning how to make nanoporous structures on purpose but also that the formation of solvate crystals can be exploited to achieve crystallisation of otherwise elusive unsolvated materials. Controlled solvent removal is investigated by several authors. For example, Ciani *et al.*[13] study dehydration of the interpenetrated polymeric species $[Cu(bpe)(SO_4)]\cdot 5H_2O$ (bpe = 1,2-bis(4-pyridyl)-ethane) while Grepioni *et al.*[27] study step-wise dehydration of the crystals of the neutral organometallic zwitterion $[Co(C_5H_4COOH)(C_5H_4COO)]\cdot 3H_2O$. It has been shown that solvent removal can be followed by thermogravimetry (TGA) experiments and that the variation (or persistence) of the crystal structures, indicative of the robustness of the networks, can be followed by powder X-ray diffraction. In the first case, the co-ordination network releases water molecules reversibly at *ca.* 393 K, with the sample after desolvation retaining essentially the same structure as the solvated species. In the organometallic case, on the other hand, the loss (above 378 K) of the first water molecule is fully reversible while complete removal of all water molecules is followed by an irreversible phase transition to crystals of the anhydrous form $[Co(C_5H_4COOH)(C_5H_4COO)]$.

One of the most striking results in the study of absorption–desorption of guest molecules from crystalline networks is reported by van Koten[33] and collaborators. It is shown that crystalline arylplatinum complexes containing N,C,N terdentate ligands reversibly bind SO_2 in the solid state. The process implies the formation of a five co-ordinate adduct. Absorption and desorption are fully reversible and occur *via* crystal-to-crystal transformations accompanied by expansion and shrinkage of the crystal structure. The Pt-complexes can thus be ragarded as supermolecules that can switch "on" and "off" as a direct response to gas uptake. Interestingly, van Koten's system, though capable of reversible gas uptake, does not possess a channelled structure. This seems to suggest that zeolitic-like characteristics are not necessary conditions for nanoporosity.

Another relevant group of solid state properties that depend directly on the topologic and electronic features of the component building blocks are those related to magnetism. Magnets based on molecular building blocks permit us to combine the magnetic behaviour of organic species (the ligands) with those of the metallic centres. The ample choice of transition metal atoms, with or without unpaired spin systems and the possibility of communication between the spin centres in the crystal architecture make magnetic properties particularly amenable to crystal engineering strategies. The number of unpaired electrons and the strength of spin coupling dictate the magnetic behaviour, *e.g.* the type of coupling as well as the magnetic ordering phenomena. The development of new molecular-based magnets strongly depends on the success of rational solid state design techniques.

Gatteschi and collaborators[34] show how the design of one-dimensional magnetic materials can benefit from the utilisation of crystal engineering methods. The goal is that of obtaining chains of different shapes by utilising paramagnetic ligands and metal centres. The candidate ligands are the aromatic nitrosyl nitroxide (NIT) ligands shown in Scheme 2 together with hexafluoroacetylacetonate M(II) complexes (M = Mn, Ni, Co, Zn, Cu). The radical ligands act as bridges between metal centres forming 1-D polymers. The shape of the chain is determined by the type of substituents. Since the magnetic ordering seems to depend on inter-chain dipolar interactions, the packing is expected to affect the ordering phenomenon, in particular the transition temperature. The comparison between the Mn complexes obtained with the ligands NITPhMe and NITPhOMe shows that packing differences (zig-zag and helical superstructures, respectively) between the two otherwise chemically very similar compounds can induce differences of the order of 50% in the critical temperatures of the two systems.



Scheme 2 Reproduced from ref. 34.

Several research papers deal with magnetic materials. Bellitto *et al.*[35] report the synthesis and characterisation by means of thermogravimetric analysis, UV-visible and IR spectroscopy, and magnetometry of iron phosphonates which show weak ferromagnetism. Spin canting and ferromagnetic ordering is also shown by the isomorphous Fe(II) and Co(II) azabenzimidazolato polymers prepared by Thompson, Storr and collaborators.[36] The compounds form diamandoid networks where tetrahedrally co-ordinated metal ions are linked by imidazolate bridges. Miller *et al.*,[37] on the other hand, prepare and characterise structurally and magnetically the metalloporphyrin charge-transfer complexes obtained with the radical anion TCNE (tetracyanoethenide) and discuss the effect of solvent on the ferrimagnetic behaviour. Differences in magnetic behaviour between polymorphs and pseudo-polymorphs arising from solvent molecule encapsulation in the crystal structures have also been discussed. The strategy employed by Coronado *et al.*[38] is based on the preparation of hybrid molecular systems in which two or three different metal centres are utilised simultaneously. The framework structure is constructed by means of M^I/M^{II} oxalato bridged networks, while decamethylferrocenium cations occupy the cavities of the superstructures.

Finally, it is worth mentioning that crystalline materials are widely employed in devices for non-linear optics and second harmonic generation. An attempt to prepare polar solids for NLO applications is discussed by Lin and Evans[16] who utilise Cd(II) metal centres bridged *via* pyridinecarboxylate ligands. Photochemistry can also afford interesting results and appears to be full of potential in inorganic crystal engineering. Balzani *et al.*[40] describe the interaction of protons and of bivalent transition metal cations with a polisydyn dendrimer. Dendrimers are macromolecules with complex tree-like structures. The interaction between cations and the dansyl groups in the superstructure is shown to have a profound influence on the fluorescence properties of the dendrimer with significant signal amplification effects. Though far from the order of the crystalline state, the study of dendrimers may pave the way to the design of fluorescent solid state chemosensors.

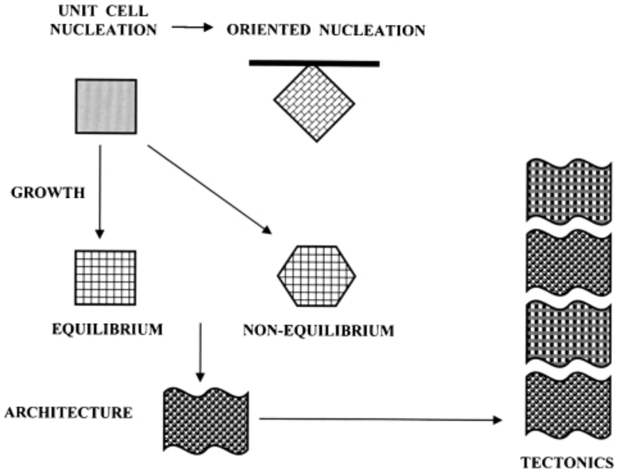


Fig. 4 Inter-relationships between crystallisation (nucleation, growth, morphology), crystal architecture (complex form) and crystal tectonics (higher-order assembly). Levels of complexity, organisation and informational content tend to increase as the length scale is extended Reproduced from ref. 41.

Crystal growth, polymorphism and biomineralisation

A major issue in ICE is that concerned with the living world. Man has always investigated, mimicked, and used Nature for man-defined objectives. However one could say that "Nature knows better". Nature knows how to build extremely sophisticated architectures and also how to utilise covalent and non-covalent bonding in an extremely efficient way to obtain extraordinary collective properties. One needs only to envisage a sea shell, which withstands enormous hydrostatic pressures, to see what can be done with calcium carbonate and proteins, or a snow flake or an iceberg to see what can be done with hydrogen bonds only. The natural world is full of specialised inorganic materials which are constructed, indeed *engineered*, to exert specific functions. Many bioinorganic materials result from the interaction of the organic components with inorganic minerals.

As well illustrated by Mann and collaborators[41] the study of *crystal tectonics* is inspired in part by the investigation of certain biological minerals which have higher-order structures that originate from the organised assembly of preformed mineral building blocks in association with organic structures such as phospholipid vesicles. The central assumption of Mann's crystal tectonics is to construct chemically materials with long range organisations that emulate the complexity and functionality of biomineralised structures. The basic idea is that of organising crystals rather than molecules or ions by utilising preformed nanoparticles to construct ordered materials (see Fig. 4).

Calcium carbonate is one of the most important biominerals, present in shells, corals, sea urchin spines, *etc.* Small calcite crystals are present inside the human ear and act as gravity devices. Although most of the calcium carbonate formed in biological systems has either the aragonite or the calcite structure, some organisms are known to be able to synthesise vaterite, which is the least thermodynamically stable form of calcium carbonate.

Crystalline inorganic materials have also important applications in optics, microelectronics, biomedical implants, separation technologies and catalysis. Aizenberg[42] shows how to deposit crystalline calcite in patterned calcite films

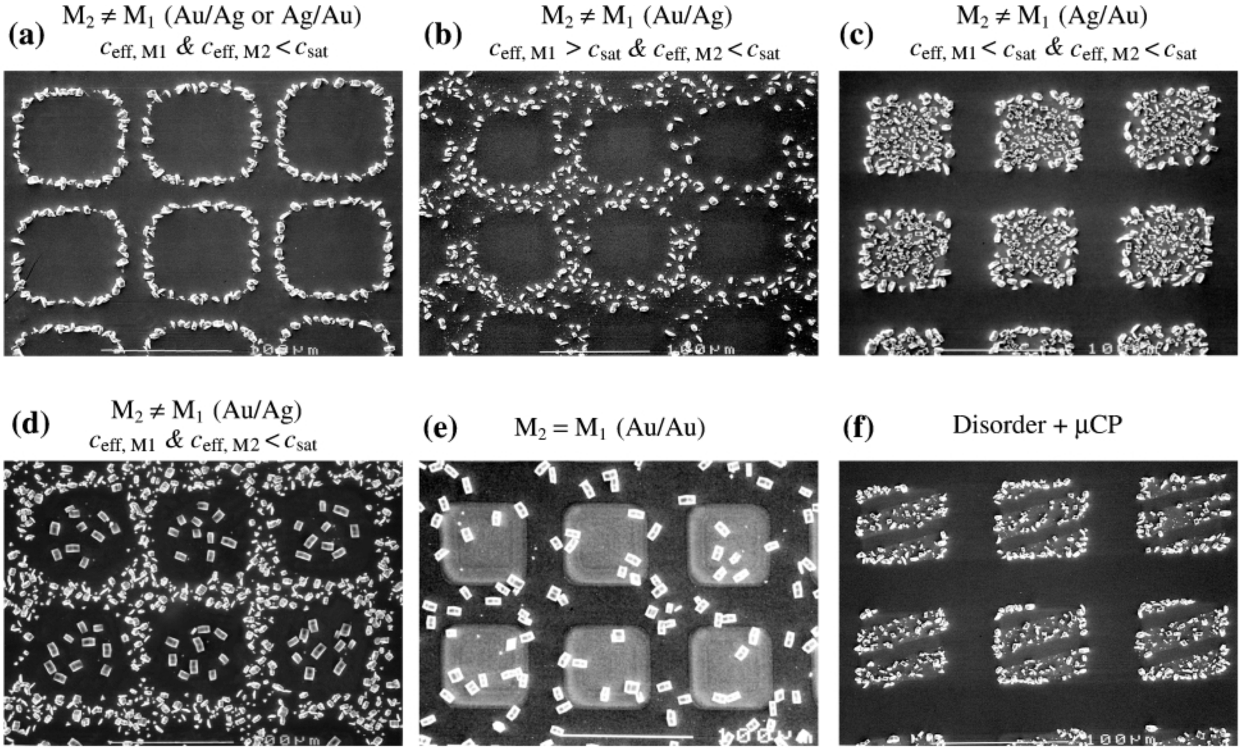


Fig. 5 (a)–(d) Patterned calcite formation on SAMs of $HS(CH_2)_{15}CO_2H$ supported on substrates that were micropatterned with Au and Ag using a stencil mask (TEM grid). The sequence of metal deposition and the concentration are indicated. Note the differences in the densities of nucleation, sizes and crystallographic orientation of crystals grown on different metals. (e) Non-patterned nucleation of oriented calcite crystals on SAMs of $HS(CH_2)_{15}CO_2H$ supported on the gold substrate micropatterned with the gold islands. (f) Complex ornament of crystals formed on a mixed metal substrate further patterened using μCP. Reproduced from ref. 42.

by using templating self-assembled monolayers supported on micropatterned mixed-metal substrates. These substrates were prepared, for example, by deposition of Au onto a Ag surface (or *vice versa*). It has been shown, in the case of calcium carbonate, that it is possible to fabricate arbitrary high resolution patterns of microcrystals with controlled sizes, orientation and density of nucleation by varying solution concentration and/or the features of the deposition surface. An example of the results reported by Aizenberg is provided in Fig. 5 and in colour on the front cover of this Special Issue of Dalton.

Sagi *et al.*[43] discuss the biomineralisation of amorphous calcite (using mainly X-ray absorption spectroscopy, but also TGA and SEM). Amorphous calcium carbonate, albeit unstable, is an important biomineral, being formed by a large number of organisms. The antler shaped spicules formed by the ascidian *Pyura pachidermatina* are composed of amorphous calcium carbonate stabilised for mechanical purposes. Falini *et al.*[44] report the controlled crystallisation of calcium carbonate on a collagenous matrix and discuss the possibility of calcium carbonate polymorphism. Kurth, Müller and collaborators[45] describe the preparation and characterisation of surfactant composite materials, monolayers, and Langmuir–Blodgett films formed by transition metal polyoxometallates (POM). POM surfaces can be modified with surfactants, yielding *surfactant encapsulated clusters* (SEC). These SECs form intriguing supramolecular architectures that are compared to the structures of naturally occurring capsule-forming proteins such as the iron storage protein ferritin.

One important point to note is the varied type of techniques that are used to study artificial minerals and biominerals. While co-ordination and molecular crystal engineering rely essentially on single crystal X-ray diffraction to fully characterise products, bio-inorganic crystal engineering only rarely shares the comfort of such a powerful technique; the papers quoted above show that a combination of techniques are usually required to achieve a good level of confidence. This particular aspect will be developed in the following section in a comparison with the techniques employed for structural characterisation in molecular and co-ordination crystal engineering.

The instruments of crystal engineering

Crystal engineering needs both the instruments of solution chemistry and those of solid state chemistry. The building blocks, be they neutral molecules, ions, or ligands destined to the construction of co-ordination networks, need to be synthesised, isolated and characterised as does any product of chemical synthesis. In addition to this, however, the typical crystal engineering product is a solid, most often (but not always) a crystalline solid, not necessarily well shaped and appropriately-sized single crystals immediately suitable for rapid single-crystal X-ray diffraction experiments. It is unquestionable that most of the results reported in this special issue would have been impossible without the progress in computing and diffraction tools that nowadays allow theoretical and experimental problems of great complexity to be tackled on a reasonable timescale, such as those associated with the complex molecular solids, interdigitated networks and supramolecular aggregates discussed above. Single crystal diffraction techniques, though rapid and efficient (area detector diffractometers can provide data sets at the pace of 1–2 crystals per day!), however, provide a sort of *biased* information. Only those materials that afford decent single crystals of adequate size can be handled in normal diffraction facilities.

Microcrystalline materials, let alone amorphous materials, require more effort and more sophisticated techniques. Since the products are solids, routine analytical and spectroscopic laboratory tools are much less useful than in the case of solution chemistry. In these cases, powder diffraction is, sometimes, the only way to ascertain whether the whole solid material has the same structure as that characterised by single crystal diffraction. Since the crystallisation product may not represent the most stable (thermodynamic) system, any new solid material should be subjected routinely to a DSC run in order to ascertain the possibility of phase transitions. The notion that grinding to a powder, a common method of sample preparation, may lead to solid state transformations and to formation of new polymorphic modifications could also be of some importance for the success of crystal engineering and solid state chemistry processes.[47] It can be anticipated, with a fair degree of confidence, that crystal engineering would take another "quantum leap" if routine methods were to become available for *ab initio* determination of crystal structures from high quality powder diffraction data, rather than requiring the less accessible synchrotron radiation or neutron diffraction facilities as at present.

Beside diffraction techniques, many papers report the use of calorimetric (DSC) and thermogravimetric (TGA) methods. These methods, even though still far from being "routine" inorganic chemistry tools, have become almost indispensable in crystal engineering labs with the increasing need to understand the thermodynamic stability of crystalline products and the possibility of phase transitions. The investigation of surfaces and of deposits requires, on the other hand, the use of FEM and SEM techniques. In order to be successful, any crystal engineering strategy needs not only to achieve good control on the building-up sequence that leads from molecules and ions to the desired crystalline materials, but also to gain a good knowledge of how the crystalline product behaves with respect to temperature, pressure, and mechanical stress if the materials will ever be of some practical use.

Beside experimental techniques, the papers collected in this volume show the importance of modelling and data-mining in ICE. Without the foresight of scientists such as O. Kennard and others, crystal engineers would today be deprived of one of their most efficacious tools: the possibility of cross analysis of numerical data on more than 180 000 organic and organometallic molecular crystal structures deposited in the Cambridge Structural Database. The tens of thousands of molecular crystals characterised in thousands of crystallographic laboratories, mostly in uncorrelated ways, contain collective information on the occurrence and transferability of given interaction motifs and on the "popularity" of a given supramolecular synthon.

Finally, the collection of beautiful drawings and schemes in this volume demonstrates the enormous importance of using graphic (*i.e.* analogic) information for the dissemination of crystal engineering results. One can hardly doubt that without the graphic facilities of modern computers it would have been very difficult not only to *report* results in a clear and straightforward way but also to *make discoveries* by investigating crystal architectures.

Future perspectives and challenges

Over a relatively short period of time, crystal engineering has grown from its cradle, which was essentially organic in nature, and now spans all areas of chemistry, with relevant interdisciplinary interactions with biology, informatics and physics. Crystal engineering is perceived as a working strategy, a utilitarian method. The contributions collected in this issue of *Dalton Transactions* demonstrate that inorganic crystal engineering is undergoing a tumultuous expansion. The reader of this volume has come across a number of rather unusual epithets (meccano kits, dendrimers, koilands and koilates, tectons and crystal tectonics, synthons, *etc.*) which show how difficult it is at times to convey information on complex architectures. An entirely new vocabulary needs to be written, most of it referring to analogic, structural types that the readers may more easily understand than by a description of bonds and connectivity, or of symmetry.

Even though, as this volume demonstrates, crystal engineering is being very successful and is attracting the scientific interest of very active, leading edge, scientists, we shall not "sweep problems under the carpet". Crystal engineering is also criticised. CE is regarded by some as "refurbishing of crystallography": the extraordinary development of computing and diffraction techniques mentioned above has certainly made crystallography a much more accessible (hence less challenging and less scientifically rewarding) discipline. Undoubtedly, this has driven many crystallographers, in the search for new ways to exploit their knowledge of solid state and crystal packing, towards crystal-oriented synthetic strategies. CE is also often criticised as a "combinatorial method" in which commercially available chemicals are mixed in varying stoichiometries and conditions to crystallise new crystalline materials. Since no new molecules are synthesised, one of the *dogmas* of chemistry is not fulfilled. CE is also often regarded as a new epithet to define (or re-define) a sub-area of materials chemistry, that of molecular materials, that has been under investigation for decades long before CE became a new fashionable area of investigation. As always, there is some ground for these (and other) criticisms. It is the challenge for the future to demonstrate that crystal engineering is providing a new way of *thinking chemistry*. It is clear, from many contributions collected in this volume, that chemists are beginning to realise that the shelves in their labs do not always hold the chemicals required to obtain the target material. They need thus to synthesise their building blocks.

Crystal-oriented synthetic strategies do not differ, in their essence, from classical chemical experiments in which molecules are modelled, synthetic routes devised, products characterised and their properties measured. In molecular crystal engineering these processes are, in a sense, repeated twice: first, in order to prepare the building blocks (whether molecules or ions), and then to arrange the building blocks in a desired way to attain and/or control crystal properties. This latter step invariably requires the characterisation of a solid product for which routine analytical and spectroscopic laboratory tools are much less useful than in the case of solution chemistry.

Crystal engineering will succeed when it will begin to "deliver the goods": not only "smart" crystalline materials with useful properties chosen by the crystal engineer and "implanted" into the molecular building blocks by the techniques of chemistry, but also nanoporous structures and zeotypes for catalysis in microcavities, to obtain photochemical sensors and solid state electronic *noses*, to exploit solid state reactivity and mechanical properties.

In his article, Mann[41] states "If there is a cloud on this new horizon it arises from the long acknowledged fact that the process of crystallization remains empirically based and subject to serendipity and "green fingers" ". Indeed, one cannot underestimate the relevance for any crystal engineering endeavour of the perpetual "thermodynamic–kinetic" dualism of crystal nucleation and growth. Are my crystals the most stable thermodynamic form? Will they undergo phase transitions with temperature or pressure or mechanical stress and how will physical properties be affected? Are there polymorphs and/or pseudo-polymorphs? Is there amorphous material together with crystals? It is unusual to close a paper with questions, but, in the opinion of this author, the main objective of this Dalton Discussion was that of providing answers from which new questions could arise. There is a need for systematic approaches to crystal growth and nucleation.[46] There is also a need for crystal engineers to "free themselves from the prison of Bragg's law", *i.e.* to overcome the enormous restriction posed by the need for periodicity in the distribution of atoms and molecules essential for successful diffraction experiments. Indeed, many of the most interesting materials are disordered or amorphous and require the utilisation of less traditional complementary techniques for their characterisation and evaluation. There is also a need for more theoretical work to be able to design (predict?) crystal structures and their properties. Maddox's words, quoted in the Introduction, are still essentially unchallenged.

Acknowledgements

I wish to thank the organising committee of the Dalton Discussion on *Inorganic Crystal Engineering*, Professors V. Balzani, L. Brammer, M. J. Calhorda, F. Grepioni, M. Mingos, A. G. Orpen, N. Roveri, and M. Schröder, for their contribution to the organisation of the scientific programme. It was a pleasure to collaborate with Dr G. McCann, managing editor of *Dalton Transactions*, in the preparation of this volume. I am grateful to J. Gibson and N. Morgan for their efficient administration and smooth organisation of the whole meeting. I thank the University of Bologna for a financial support that has permitted the participation of many young scientists and for providing an excellent site for the conference. I thank the Società Chimica Italiana, the Divisione di Chimica Inorganica, and the Gruppo Interdivisionale di Chimica Strutturale for their support. I thank, in particular, Professor A. Tiripicchio for his guidance. I thank Drs S. Fermani, M. Gandolfi, M. Polito, L. Maini, L. Scaccianoce and N. Zaccheroni for their help during the conference. I thank Professor Leslie Glasser, on sabbatical leave in Bologna, for useful comments concerning this manuscript. Finally, I acknowledge the Royal Society of Chemistry for having recognised crystal engineering as a strategic field of research which deserves investment and support. This foresight is witnessed by the launch of the new RSC journal *CrystEngComm* devoted to crystal engineering, and, of course, by the financial and technical support provided to the organisation of this Dalton Discussion.

References

1 G. M. J. Schmidt, *Pure Appl. Chem.*, 1971, **27**, 647.
2 J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1304; J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995.
3 M. C. Etter, *J. Am. Chem. Soc.*, 1987, **109**, 7786.
4 J. Maddox, *Nature*, 1988, **335**, 201.
5 G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Elsevier, Amsterdam, 1989.
6 D. Braga, *Chem. Rev.*, 1992, **92**, 633.
7 See, for a general entry: *Crystal Engineering: from Molecules and Crystals to Materials*, D. Braga, F. Grepioni and A. G. Orpen, eds., Kluwer Academic Publishers, Dordrecht, 1999.
8 D. Braga and F. Grepioni, *Acc. Chem. Res.*, 2000, **33**, 601.
9 S. J. Cantrill, A. R. Pease and J. F. Stoddart, *J. Chem. Soc., Dalton Trans.*, 2000, 3715.
10 R. Robson, *J. Chem. Soc., Dalton Trans.*, 2000, 3735.
11 K. Biradha and M. Fujita, *J. Chem. Soc., Dalton Trans.*, 2000, 3805.
12 A. J. Blake, N. R. Champness, P. A. Cooke, J. E. B. Nicolson and C. Wilson, *J. Chem. Soc., Dalton Trans.*, 2000, 3811.
13 L. Carlucci, G. Ciani, D. M. Prosperpio and S. Rizzato, *J. Chem. Soc., Dalton Trans.*, 2000, 3821.
14 S. R. Batten, A. R. Harris, P. Jensen, K. S. Murray and A. Ziebell, *J. Chem. Soc., Dalton Trans.*, 2000, 3829.
15 K. Biradha, A. Mondal, B. Moulton and M. J. Zaworotko, *J. Chem. Soc., Dalton Trans.*, 2000, 3837.
16 O. R. Evans and W. Lin, *J. Chem. Soc., Dalton Trans.*, 2000, 3949.
17 G. R. Desiraju, *J. Chem. Soc., Dalton Trans.*, 2000, 3745.
18 D. Braga, F. Grepioni and G. R. Desiraju, *Chem. Rev.*, 1998, **98**, 1375.
19 F. H. Allen and O. Kennard, *Chem. Des. Automat. News*, 1993, **8**, 31.
20 H. A. Miller, N. Laing, S. Parsons, A. Parkin, P. A. Tasker and D. J. White, *J. Chem. Soc., Dalton Trans.*, 2000, 3773.
21 X. Xu, S. L. James, D. M. P. Mingos, A. J. P. White and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 2000, 3783.
22 A. D. Burrows, R. W. Harrington, M. F. Mahon and C. E. Price, *J. Chem. Soc., Dalton Trans.*, 2000, 3845.
23 L. Brammer, J. C. M. Rivas, R. Atencio, S. Fang and F. C. Pigge, *J. Chem. Soc., Dalton Trans.*, 2000, 3855.
24 C. B. Aakeröy, A. M. Beatty and K. R. Lorimer, *J. Chem. Soc., Dalton Trans.*, 2000, 3869.
25 A. J. Blake, P. Hubberstey, U. Suksangpanya and C. L. Wilson, *J. Chem. Soc., Dalton Trans.*, 2000, 3873.
26 A. L. Gillon, G. R. Lewis, A. G. Orpen, S. Rotter, J. Starbuck, X.-M. Wang, Y. Rodriguez-Martin and C. Ruiz-Pérez, *J. Chem. Soc., Dalton Trans.*, 2000, 3897.
27 D. Braga, G. Cojazzi, A. Abati, L. Maini, M. Polito, L. Scaccianoce and F. Grepioni, *J. Chem. Soc., Dalton Trans.*, 2000, 3969.
28 C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2000, 3885.
29 P. Pyykkö, *Chem. Rev.*, 1997, **97**, 597.
30 T. Mathieson, A. Schier and H. Schmidbaur, *J. Chem. Soc., Dalton Trans.*, 2000, 3881.
31 J. Martz, E. Graf, M. W. Hosseini, A. De Cian and J. Fischer, *J. Chem. Soc., Dalton Trans.*, 2000, 3791.
32 S. Bordiga, I. Roggiero, P. Ugliengo, A. Zecchina, V. Bolis, G. Artoli, R. Buzzoni, G. Marra, F. Rivetti, G. Spanò and C. Lamberti, *J. Chem. Soc., Dalton Trans.*, 2000, 3921.
33 M. Albrecht, M. Lutz, A. M. M. Schreurs, E. T. H. Lutz, A. L. Spek and G. van Koten, *J. Chem. Soc., Dalton Trans.*, 2000, 3797.
34 A. Caneshi, D. Gatteschi, N. Lalioti, C. Sangregorio and R. Sessoli, *J. Chem. Soc., Dalton Trans.*, 2000, 3907.
35 A. Altomare, C. Bellitto, S. A. Ibrahim, M. R. Mahmoud and R. Rizzi, *J. Chem. Soc., Dalton Trans.*, 2000, 3913.
36 S. J. Rettig, V. Sánchez, A. Storr, R. C. Thompson and J. Trotter, *J. Chem. Soc., Dalton Trans.*, 2000, 3931.
37 D. K. Rittenberg, A. M. Arif and J. S. Miller, *J. Chem. Soc., Dalton Trans.*, 2000, 3939.
38 E. Coronado, M. Clemente-León, J. R. Galán-Mascarós, C. Giménez-Saiz, C. J. Gómez-García and E. Martínez-Ferrero, *J. Chem. Soc., Dalton Trans.*, 2000, 3955.
39 See, for example, S. R. Marder, *Inorg. Mater.*, 1992, 115; N. J. Long, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 21; D. R. Kanis, M. A. Ratner and T. J. Marks, *Chem. Rev.*, 1994, **94**, 195.
40 V. Balzani, P. Ceroni, S. Gestermann, M. Gorka, C. Kauffmann and F. Vögtle, *J. Chem. Soc., Dalton Trans.*, 2000, 3765.
41 S. Mann, S. A. Davis, S. R. Hall, M. Li, K. H. Rhodes, W. Shenton, S. Vaucher and B. Zhang, *J. Chem. Soc., Dalton Trans.*, 2000, 3753.
42 J. Aizenberg, *J. Chem. Soc., Dalton Trans.*, 2000, 3963.
43 Y. Levi-Kalisman, S. Raz, S. Weiner, L. Addadi and I. Sagi, *J. Chem. Soc., Dalton Trans.*, 2000, 3977.
44 G. Falini, S. Fermani, M. Gazzano and A. Ripamonti, *J. Chem. Soc., Dalton Trans.*, 2000, 3983.
45 D. G. Kurth, P. Lehmann, D. Volkmer, A. Müller and D. Schwahn, *J. Chem. Soc., Dalton Trans.*, 2000, 3989.
46 J. Dunitz and J. Bernstein, *Acc. Chem. Res.*, 1995, **28**, 193; N. Bladgen and R. J. Davey, *Chem. Br.*, 1999, **35**, 44; D. Braga and F. Grepioni, *Chem. Soc. Rev.*, 2000, **29**, 229.