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Glorious uncertainty—challenges for network design

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Abstract

This article discusses the challenges that face the crystal engineer in the deliberate design of new network structures. These include control over ligand and metal coordination geometry, selection of network topology from a number of possibilities which all have the same connectivity, and control of methods of increasing packing efficiency, including interpenetration (both number of nets (including only one) and topology of interpenetration). These variables can lead to polymorphism and related phenomena, the bane of crystal engineers. Templation by counterions, guest molecules and/or solvents can also lead to unpredictable results.

Keywords: Coordination polymers; Crystal engineering; Topology; Networks; Polymorphs; Interpenetration; Hydrogen bonding

An effective and widely used strategy for the design of coordination polymers, based on the selection of metal and ligand geometries to produce given network topologies, has been around for some 15 years now [1]. This strategy can be highly rewarding, allowing, for example, the targeting of certain network topologies (e.g. diamond) which are likely to produce acentric structures [2], the design of magnetically interesting nets such as the Kagomé lattice [3], or the synthesis of highly porous materials [4]. Despite this, however, the crystal engineering of coordination polymers can still be a highly unpredictable pursuit [5]. Thus, it is timely to discuss a number of the current challenges for the network designer, including some examples from our own studies.

The first challenge is to coax the building blocks (metals and ligands) to behave as predicted. This may sound trivial, but it many cases it is not. Flexible ligands can be particularly difficult to predict their final geometry, but even rigid ligands can refuse to coordinate, or can show multiple bonding modes. For example, the azide ligand commonly displays $\mu_{1,3}$ and $\mu_{1,1}$ bonding modes, among others [6]. The bonding mode displayed is particularly important as the $\mu_{1,3}$ coordination mode generally produces antiferromagnetic coupling between metal ions, while the $\mu_{1,1}$ mode usually produces ferromagnetic coupling [6]. Dicyanamide (dca, $N(CN)_2^-$) is another magnetically interesting ligand which shows a variety of coordination modes [7]. The most common is a bidentate $\mu_{1,5}$ bridging mode; however, more interesting (and more difficult to achieve) is the tridentate $\mu_{1,3,5}$ bridging mode, which is more likely to produce magnetically ordering structures [7]. Metal coordination geometries can also unpredictable, particularly for those malleable metal ions which possess two or more common coordination geometries, such as Cu(I), Cu(II), Zn(II), Ag(I) or Cd(II). As an illustration of these uncertainties, compare the structures of ZnL_2, $L =$ dca or tcm, tcm = tricyanomethanide, $C(CN)_3^-$ [7]. Both ligands can coordinate in a tridentate fashion, and octahedral geometry is common for the Zn(II) ion. Both these coordination modes are found in the structures of ML_2, $M =$ Cr, Mn, Fe, Co, Ni, Cu [7]. However, while $Zn(tcm)_2$ contains trigonal ligands and octahedral metal ions, generating two

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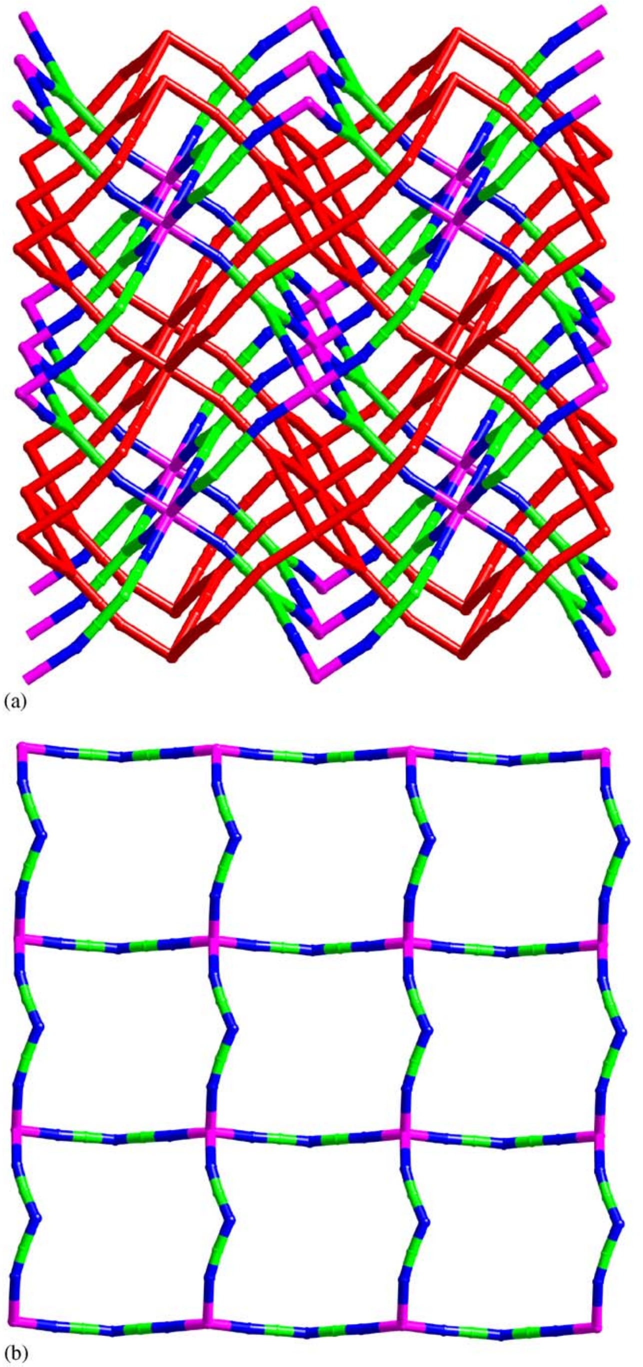

Fig. 1. (a) The two interpenetrating rutile-related 3D nets of $Zn(tcm)_2$, tcm = tricyanomethanide, $C(CN)_3^-$. (b) The 2D (4,4) sheet structure of $Zn(dca)_2$, dca = dicyanamide, $N(CN)_2^-$.

interpenetrating 3D rutile-related structures, $Zn(dca)_2$ contains tetrahedral metal ions and bidentate ligands, creating 2D (4,4) sheets (Fig. 1).

Even if the ligand and metal ion coordination geometries are correctly predicted, further complications can arise. There are, for example, numerous networks possible with only 3-connecting nodes [8,9]. These can range from 1D (e.g. ladders) to 2D ((6,3) sheets) to 3D (e.g. (8,3)-*c*, (10,3)-*a*, (10,3)-*b*, (12,3), and so forth). Thus, controlling the local coordination geometries controls only this; the overall network topology is still out of our complete control. Even for tetrahedrally connected networks, where diamond is the overwhelmingly dominant topology, the question remains: *why?* There are other perfectly feasible nets possible for tetrahedral nodes, such as Lonsdaleite and quartz. Why is diamond so special? The answer may lie in the high underlying symmetry of the net [10] as it is the most highly symmetric and simplest of the nets containing tetrahedral nodes. Indeed it has been argued, quite reasonably, that the diamond net is the 'default' topology for tetrahedral nodes [10]. Even low-symmetry structures with asymmetric or flexible ligands or nodes form this net regularly. Nonetheless, even for tetrahedral nodes, other network topologies are possible and have been formed.

A further complication can arise for networks with significant cavities and channels: *how are these filled?* For 2D (and 1D) networks, there are three main ways in which the packing efficiency can be maximised: interdigitation, interpenetration and intercalation [11], and which method (or combination of methods) occurs can be affected by subtleties. Reaction of Cu(I), tcm and either hexamethylenetetramine (hmt), 4,4′-bipyridine (bipy), or 1,2-bis(4-pyridyl)ethene (bpe) results in (4,4) sheets with bridging bidentate ligands but different packing modes [11]. The structure of Cu(tcm)(hmt) shows interdigitation of adjacent sheets, Cu(tcm)(bipy) contains layers of doubly interpenetrating sheets which then interdigitate, while in Cu(tcm)(bpe) · 1/4bpe · 1/2MeCN the sheets stack to give channels which contain intercalated bpe and MeCN molecules (Fig. 2).

Interpenetration also provides its own complications. The first question is: *will it occur, and if so, how many nets?* We have already seen an example of three related 2D structures in which interpenetration occurs for only one. A classic example for 3D nets are the diamondoid structures of $Cd(CN)_2$ and Cu[4,4′,4″,4‴-tetracyanophenylmethane]$BF_4 \cdot xC_6H_5NO_2$ [1]. In the former, the node-to-node distance is 5.46 Å, and two nets interpenetrate. In the latter, the node-to-node distance is 8.86 Å, but only one net is formed, which occupies only about a third of the crystal volume. Yaghi et al. have reported a series of 3D nets with α-Po structures with clusters as nodes which can occur as both highly porous single nets, and structures with two interpenetrating networks [12]. This fascinating phenomenon, which is appears to be dependant on reaction concentration, deserves further study to fully examine the production of interpenetrating versus non-interpenetrating structures. The final example comes from a study of hydrogen bonded nets. The molecule 3,3′,5,5′-tetramethyl-4,4′-bipyrazole (Me_4bpz) forms six interpenetrating (10,3)-a nets in the γ phase and methanol solvate,

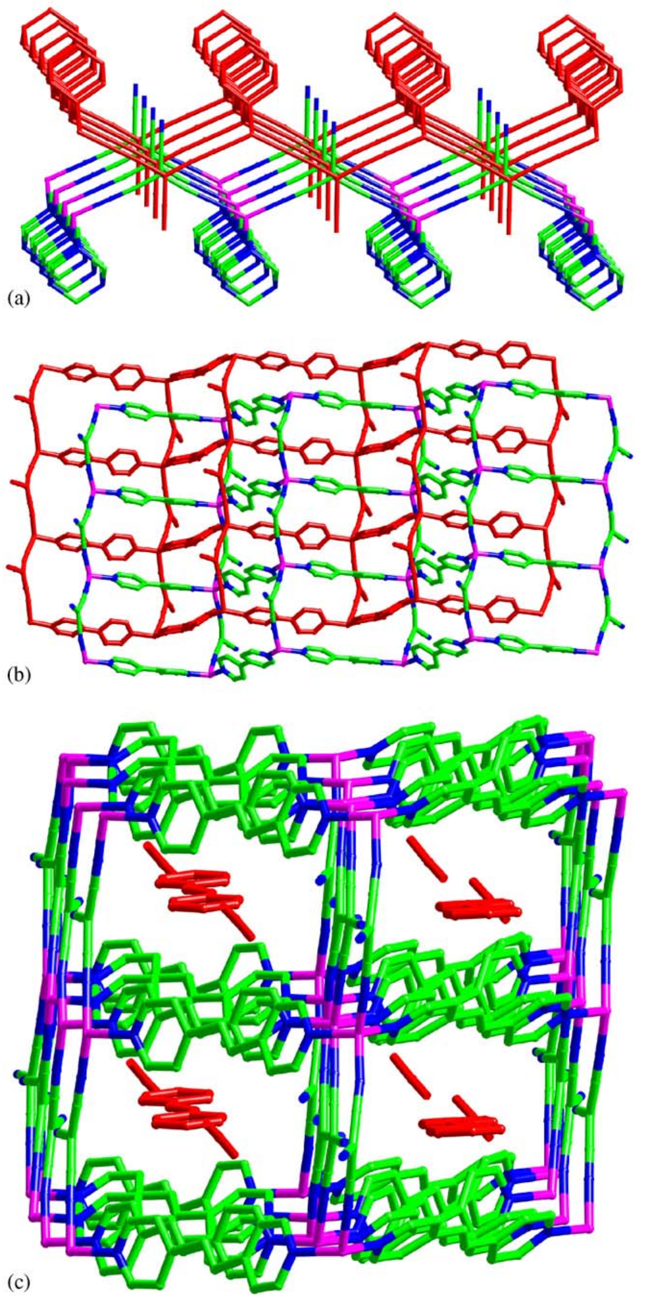

Fig. 2. (a) Interdigitation in the structure of Cu(tcm)(hmt), hmt = hexamethylenetetramine. (b) Interpenetration in the structure of Cu(tcm)(bipy), bipy = 4,4′-bipyridine. (c) Intercalation in the structure of Cu(tcm)(bpe) · 1/4bpe · 1/2MeCN, bpe = 1,2-bis(4-pyridyl) ethene.

but only four in the chloroform solvate [13]. This system also reinforces the earlier discussion on multiple nets possible with given node geometries—the α phase of Me$_4$bpz forms (10,3)-*b* nets, while the β polymorph has (10,3)-*c* nets [14].

The mode of interpenetration is another possible variable. For example, 2D networks can show parallel or inclined interpenetration [15]. Even 3D networks can show different interpenetration topologies—although diamond and α-Po nets usually display a particular way of interpenetrating, other, 'abnormal' topologies of interpenetration have been observed [16].

All these factors contribute to the formation of polymorphs, which encapsulate the challenges of structure prediction or design for the crystal engineer. For example, the reaction of Cu(I), dca and bpe in MeCN results in formation of both orange and dark red crystals [17]. Both crystals contain Cu(dca)(bpe) coordination nets in which tetrahedral Cu(I) ions are bridged by bidentate dca and bpe bridges. However, the orange crystals (α-Cu(dca)(bpe)) contain layers of doubly interpenetrating 2D (4,4) sheets, while the dark red crystals (β-Cu(dca)(bpe)) contain five interpenetrating diamond nets (Fig. 3). Thus, even when the local coordination geometries of the metals and ligands are identical, very different networks can be produced. The same reaction with the bipy ligand in place of bpe [17] provides another interesting example which is analogous to pseudopolymorphism, whereby structures differ in the numbers or types of included solvent molecules [18]. It also illustrates the problems of kinetic versus

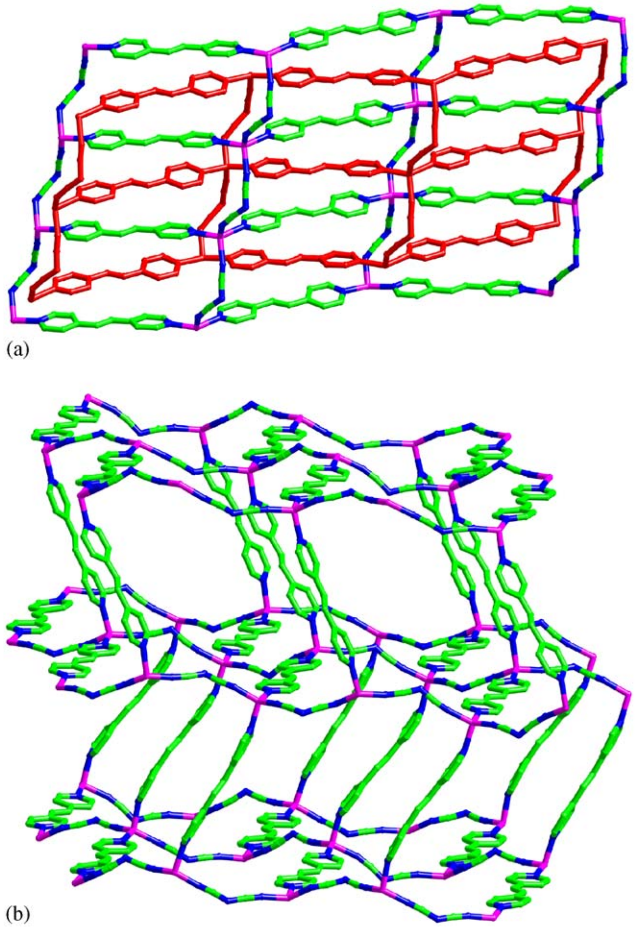

Fig. 3. (a) Doubly interpenetrating 2D (4,4) sheets in the structure of α-Cu(dca)(bpe). (b) One of the five interpenetrating diamondoid nets in the structure of β-Cu(dca)(bpe).

thermodynamic products. The reaction initially produces yellow–orange dichroic crystals, however these disappear after 1–3 days and are replaced by (presumably) more thermodynamically stable dark red crystals. The yellow–orange crystals have the formula $Cu_2(dca)_2(bipy)(MeCN)_2 \cdot 0.5bipy$. The structure consists of 1D ladders with intercalated bipy molecules. The dark red crystals, $Cu_4(dca)_4(bipy)_3(MeCN)_2$, contain 'thick' 2D layers which show 2D→3D parallel interpenetration [16]. Despite the different structures, the formulae of the two compounds differ only in the number of coordinated MeCN solvent molecules, which are in large excess for these reaction conditions anyway. Note also, despite only a modest increase in the ligand length, the difference between the bpe and bipy structures, and, indeed, the differences in comparison to the aforementioned tcm analogues. True network design, even with the aid of closely related structures, can be tough!

Related to the problem of polymorphism is structure templation of network topology by counterions, solvents or guest molecules. Modest variation of one of these variables can result in very different structures. Cation templation is a good example. Anionic metal oxalate networks form (6,3) sheets when crystallised with tetraalkyl or tetraaryl amines or phosphines, but form chiral (10,3)-*a* 3D networks when $[M(2,2'\text{-bipyridine})_3]^{2+}$ cations are used [19]. Anionic metal dicyanamide networks are even more cation dependant. In the structures $(Ph_4E)[M(dca)_3]$, $E = P$, As, $M = Mn$, Fe, Co, Ni, 2D (4,4) sheets are formed [7,20,21]. Replacement of a single cation phenyl group with either a methyl or ethyl group results in formation of five-connected 3D networks instead [21,22]. In the reverse of the oxalate case, use of $[M(2,2'\text{-bipyridine})_3]^{2+}$ cations results in formation of 2D (6,3) nets [23], while $[(C_5Me_5)_2Fe]^+$ cations result in α-Po network formation [24].

The solvent also plays a vital role in structure design. The first question to be answered is: *will the solvent coordinate, be intercalated, or be ignored in the crystallisation process?* If the solvent is not ignored, then it can have a crucial structure-directing effect. For example, the structures of cadmium cyanide solvates are very dependant on the solvent, which may either coordinate or be intercalated. Reaction of cadmium and cyanide in water gives $Cd(CN)_2$, which, as discussed above, has two interpenetrating diamond nets [1]. Crystallisation of $Cd(CN)_2$ from CCl_4, however, gives $Cd(CN)_2 \cdot CCl_4$ [25]. This structure has only one diamond-like network, with CCl_4 molecules occupying the cavities. The structure of $Cd(CN)_2 \cdot 0.5(n\text{-}Bu_2O \cdot H_2O)$ is a rare example of Lonsdaleite topology [26], while $Cd(CN)_2 \cdot 2/3H_2O \cdot t\text{-}BuOH$ has a moganite topology in which one third of the Cd centres are now octahedral (rather than tetrahedral) through coordination of water ligands [27]. Numerous other cadmium cyanide networks have be obtained through variation of solvent [28]. Finally, reaction conditions, such as the temperature of hydrothermal synthesis [29], or even the use of hydrothermal conditions versus room temperature and pressure reactions, can greatly affect the nature of the products obtained.

Despite these important challenges for the future, there is no doubt the modular, net-based approach is an essential part of crystal engineering, for both the design and analysis of crystal structures (including both coordination polymers and hydrogen bonded networks). It has produced some spectacular and fascinating results, and will continue to do so for the foreseeable future. However, despite the increasing number of examples of true structure design, we should not be blind to the limitations and challenges of this approach. We can, at best, direct rather than predict structures—i.e. we can create the conditions under which our desired structure is possible, but we cannot be certain of its formation. This is nonetheless a considerable achievement, and its significance should not be underestimated. However, this area is still very much an experimental pursuit, with surprises and subtleties at every turn. This is not necessarily a bad thing—while we aim to predict and understand, the most enjoyable and rewarding structures are often those we did not expect.

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