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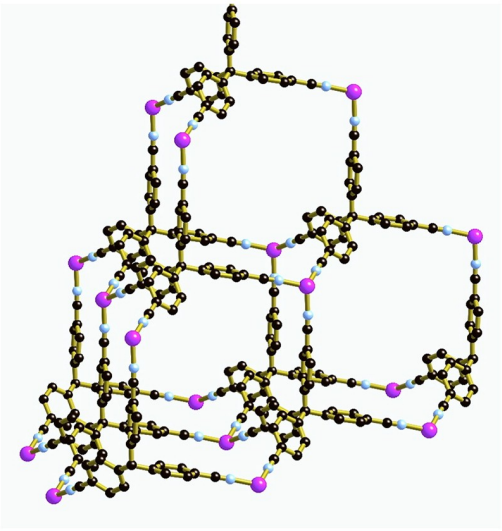
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The Historical Development of the Concepts Underlying the Design and Construction of Targeted Coordination Polymers/MOFs: A Personal Account

Richard Robson*[a]

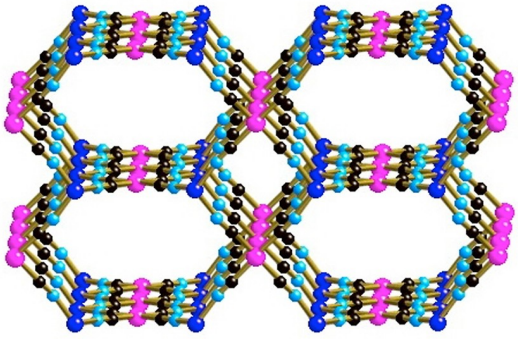
Diamond topology

1989



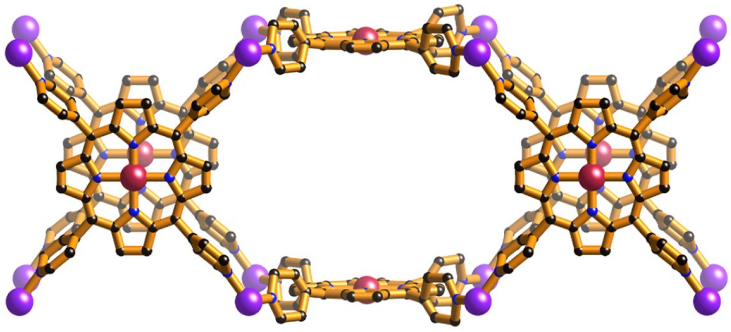
PtS topology with $[Pt(CN)_4]^{2-}$ building blocks

1990



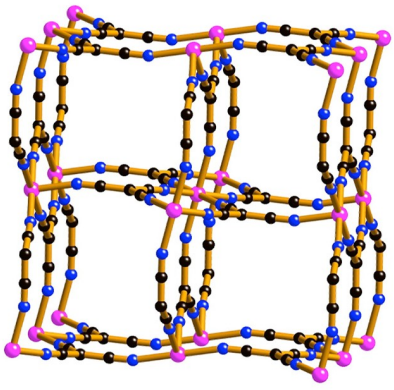
PtS topology with porphyrin building blocks

1994



Rutile topology

1991



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Abstract: Presented here is a personal account of how the ideas and concepts underlying the design and construction of coordination polymers/MOFs developed historically - from the earliest conjectures in the 1970's about the possibility of using pre-organized building blocks to construct targeted polymeric structures, to the initial experimental implementation of these ideas in the mid-80's and to the introduction of the name MOFs in the 90's. The early exploratory work with pre-organized building blocks described in this article paved the way for the subsequent explosion of research activity in the CP/MOF area and for the generation of an essentially unlimited range of designed coordination polymer structures promising a variety of useful properties.

Keywords: coordination polymer, materials science, MOF, pre-organisation, science history

1. Introduction

1.1. Pre-Organization

A central theme in this article is pre-organization – the design of functionality and geometry in reactant species that predisposes them, when they are brought together, to form bonds in a specific, intended manner, leading to the spontaneous assembly of a targeted structure. On becoming an independent researcher in 1966 the approach to discovering new chemistry that I chose to follow was based on this notion of pre-organisation - commonplace now but not so then. I took much ecouragement at that time from the insights that were emerging into the structure and function of metalloproteins – marvellously efficient systems pre-organized by nature.

2. Discussion

2.1. Pre-Organized Building Blocks Generating Discrete Coordination Complexes

I devised ligands, given the name binucleating ligands,[1] capable of securing two metal centres in very close proximity; the metal complexes of these pre-organized ligands offered prospects of new types of reactivity at the bimetallic site, new catalysts, new types of metal-metal electronic interaction and useful parallels with certain metalloproteins. During the ensuing two decades my small group, whilst exploring these binuclear complexes, uncovered numerous examples of unprecedented structures and unusual reaction processes – all consequences of the pre-organization.[2]

I proposed that macrocycles pre-organized to bind not one metal centre but a pair in enforced close proximity might offer outstanding scope for novel chemistry. In the late 60's I isolated in crystalline form the first example of a complex of a macrocyclic binucleating ligand (a Cu^{II}_2 complex) and in 1970 we reported a family of such complexes with a number of different transition metals.[3] Binuclear complexes of these types have since attracted much attention. Recently, macrocyclic bimetallic species that catalyse efficient CO_2/epoxide copolymerisation to yield polycarbonates as well as catalysts for chemical recycling have been reported.[4]

In the 80's we reported macrocyclic ligands pre-organized to secure four metal centres in very close proximity,[5] the properties and reactivity of which still await exploration because we re-directed our limited resources to coordination polymer work (described below) which was showing great promise at that time.

2.2. Pre-organized Building Blocks for the Construction of Coordination Polymers by Design

In 1974 I was given the job of building ball and stick models of several basic inorganic structures for first year lecture demonstrations. Whilst assembling the models, with ideas about pre-organization in the research we had underway at that time active at the back of my mind, the question arose - "If we were to substitute molecules for balls and chemical bonds for rods/sticks, might it be possible that appropriately functionalized, pre-organized building blocks would undergo spontaneous reaction to assemble themselves into extended networks of targeted structure?" For example, the rutile (TiO_2) model consisted of trigonal 3-connecting balls (representing O) connected by rods to octahedral 6-connecting balls (representing Ti). The question that arose was "If we had at our disposal appropriately pre-organized trigonally functionalised, 3-connecting molecular units and octahedrally functionalised 6-connecting units, would the two, when brought together, spontaneously yield a rutile-related network?"

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A decade was to pass before I sarted benchwork to test out these ideas, at a time when this was a natural extension of the binuclear and tetranuclear work. I chose the diamond-related network as the target for my first attempts. I synthesised the tetranitrile [C(p-$C_6H_4CN)_4$], with the aim of combining this with Cu(I). The intention here was that Cu(I) would take on a tetrahedrally-disposed set of nitrile donors from four separate tetranitrile components. The tetranitrile was in turn intended to bind four Cu(I) centres at the corners of a tetrahedron, with more or less linear geometries anticipated at the nitrile carbon and nitrogen atoms. The hope was that a very spacious diamond-like network would be generated in this way. At that time (the late 80's) any reasonable chemist would have rated the chances of success in this venture as remote indeed. Ill-defined, amorphous precipitates, consisting of tangled birds nests of the components, difficult or impossible to characterise, seemed much more likely outcomes than the single crystals suitable for X-ray diffraction studies that were required. As it turned out, I did obtain suitable single crystals with amazing ease, merely by combining [$C(C_6H_4\cdot CN)_4$] in nitrobenzene with $Cu(CH_3CN)_4BF_4$ in acetonitrile and allowing the mixture to evaporate partially. Selective loss of the more volatile acetonitrile was intended to allow the tetranitrile to compete increasingly effectively with the acetonitrile for coordination to copper, thereby feeding the growing polymeric network. The structural features of the solvated $Cu^I[C(C_6H_4.CN)_4]BF_4$ product, determined by my crystallographer colleague, Bernard Hoskins, were almost exactly as intended.[6] The 3D cationic $\{Cu^I[C(C_6H_4.CN)_4)]\}^+$ network had the very open diamond-like connectivity seen in Figure 1. This network occupied less than half the volume of the crystal, the large intra-framework spaces being filled by highly disordered solvent molecules together with mobile BF_4^-. Significantly, single crystals survived anion exchange, retaining their single crystal character. At that time, this was a most unusual material - one that was undoubtedly crystalline and yet more than half its contents by volume were essentially liquid.

In the paper reporting these results,[6] we also proposed a much more general, wider ranging approach to the construction of what we anticipated might be a very extensive new class of coordination polymer networks that might provide useful tailor-made materials of the future. A number of general observations, postulates and predictions were made in that paper that seemed likely to be of relevance in the (anticipated) future development of the coordination polymer field:

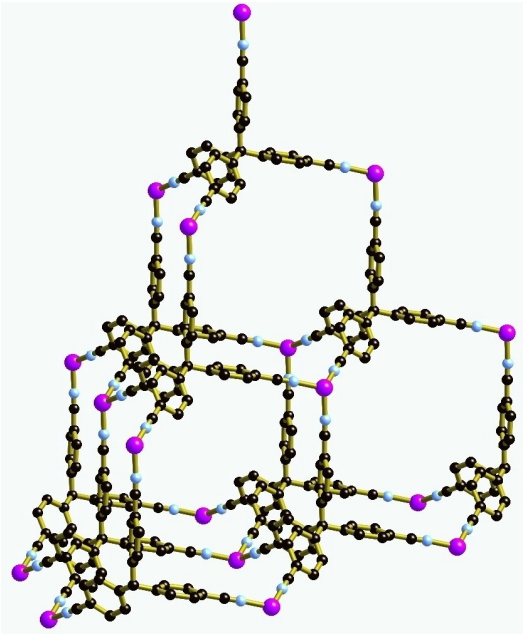


Figure 1. Part of the diamond-like $\{Cu^I[C(C_6H_4\cdot CN)_4]\}^+$ network.

(1) Given the limitless range of connecting ligands that could be readily imagined and synthesised (with all sorts of geometries, connectivities and functionalities) and given also the rich geometrical and electronic diversity of metallic elements, it was clear that coordination polymers, if they could be generally obtained in crystalline form as easily as I had obtained $Cu^I[C(C_6H_4.CN)_4]BF_4$ could afford an enormous range of porous solids resembling zeolites but with a much greater diversity of architectures and properties.
(2) The polymers envisaged might provide–quote: "materials combining good or even high thermal, chemical and mechanical stability with unusually low density".
(3) Functionalisation of the framework either before or after its construction to provide active sites for heterogeneous catalysis, might be straightforward.



Richard Robson grew up in Glusburn, Yorkshire where he was born in 1937. After a D.Phil. at Oxford and postdoctoral positions at Caltech and Stanford, he was appointed Lecturer in Inorganic Chemistry at the University of Melbourne in 1966 where he has worked ever since. He retired in 2004 and has since then been Professorial Fellow in the School of Chemistry at Melbourne. He is a Fellow of both the Royal Society and the Australian Academy.

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(4) It might be crucial in the growth of ordered, truly crystalline arrangements that the bond forming step whereby that growth occurs be appropriately reversible - thus, if a "wrong step" were taken the system would be able to "backtrack" to eliminate the error and then the orderly build-up could continue.
(5) Bridging ligands bearing chelating sites for metal binding might afford significantly more robust framework structures.

It has been a pleasure to witness the subsequent explosive growth of the coordination polymer/MOF field, with contributions from many researchers, that has borne out the viability of all these postulates.

Point 3 above concerning the introduction of functional groups to provide active sites for heterogeneous catalysis has been the subject of vigorous investigation by others in recent times – an area now referred to as post-synthetic modification.[7]

With regard to point 4 above concerning the importance of reversibility in the framework building, I pointed out in 1996 that it might be possible that our successful use of reversible metal-ligand bond formation for the construction of crystalline coordination polymers might be extended to the use of certain carbon-oxygen, carbon-nitrogen and carbon-carbon bond-forming steps, that were known to be reversible, to engineer truly crystalline organic (ie. metal-free) polymers.[8] This suggestion seems not to have been noticed in the subsequent development of the COF field.

The above approach to network construction was publicized in a talk given at a meeting of the ACS in Atlanta in April 1991.[9]

In the late 80's, having successfully constructed coordination polymer networks with intended diamond-related structures I was searching for other structural prototypes to be used as targets. The rutile and the PtS prototypes were immediately attractive because it was easy to conceive geometrically and functionally appropriate building blocks that were also readily available. As considered above, the components required for a rutile structure are trigonal 3-connecting units and half as many octahedral 6-connecting units. In exploratory work of this kind in which the objective was to establish principles, it seemed wise to examine the simplest possible systems first; more elaborate objectives could be investigated later if the simpler systems showed any promise - an outcome far from assured at that time. For the role of the trigonal unit the simplest I could imagine was the tricyanomethanide anion, $C(CN)_3^-$, (tcm^-). Metal centres capable of adopting an octahedral ligand geometry were obvious choices for the role of the octahedral component. In 1991 we reported that bringing Zn^{2+} and tcm^- together under the simplest conditions at room temperature produced single crystals of $Zn(tcm)_2$ which did contain the intended rutile-like network (Figure 2).[10] As can be appreciated by comparing Figure 2a with 2b the intra-framework spaces in $Zn(tcm)_2$ were much larger than those in rutile itself, so large in fact that a second, identical but independent network interpenetrated the first and *vice versa.* Eventually we reported a large family of isostructural $M^{II}(tcm)_2$ solids (M=Cr, Mn, Co, Ni, Zn, Cd and Hg) with intended rutile-related structures.[11]

In the early stages of our exploration of framework construction, I was thinking in terms of the *structures* of possible targets. Only later did I realize that the targets for

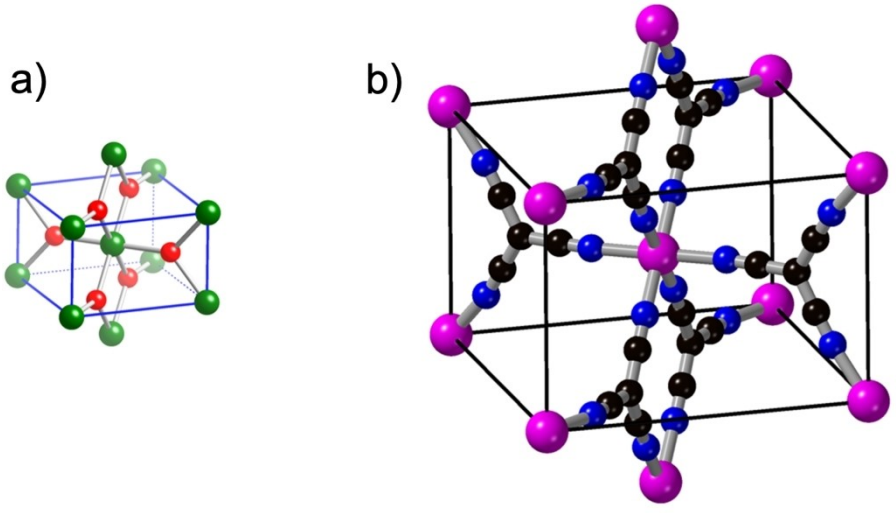


Figure 2. a) Part of the rutile, TiO_2, network b) a comparable fraction of a single rutile-like network in $Zn(tcm)_2$. Figures 2a and 2b are roughly to scale indicating how much more open the $Zn(tcm)_2$ network is compared to that in rutile.

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construction that we were seeking were really "ways of connecting things together". The relationship between the deliberately constructed rutile-like networks described above and the rutile parent is that they share the same underlying connectivity or topology, as can be clearly seen in Figure 2. These underlying connectivities are best considered in terms of the concept of nets. The book "Three Dimensional Nets and Polyhedra" by A. F. Wells, published in 1977, provides a catalogue of nets of great value to an aspiring network builder.[12]

The PtS net was an early target in our exploration of coordination polymers-by-design. In the PtS net there are equal numbers of square planar 4-connecting centres and tetrahedral 4-connecting centres each attached to four of the other type (Figure 3).

My interest in the PtS structure, from the outset, was sparked by the exciting possibility of using appropriately functionalised metalloporphyrin units to provide square planar building blocks of large size. The expectation was that the large porphyrin components would ensure that the channels within the PtS-like structure would be spacious, affording access of reactant species to potentially catalytically active porhyrin sites. It seemed wise, however, initially to postpone such ambitious porphyrin objectives and aim for the simplest possible tetrahedral and square planar components I could think of. Cu(I) was chosen for the tetrahedral role and the very stable and easily accessible $Pt(CN)_4^{2-}$ anion for the square planar role. I obtained the compound $NMe_4\{Cu^I[Pt(CN)_4]\}$in crystalline form very simply from its component ions. The anionic $\{Cu^I[Pt(CN)_4]\}^-$ 3D network did have the intended PtS-related structure (Figure 4) as was reported in 1990.[13]

This result provided much-needed encouragement that the imagined PtS-related porphyrin networks were not preposterously ambitious objectives. For the role of square planar porphyrin component I chose one pre-organized with four 4-pyridyl donors directed outwards towards the corners of a square, namely 5,10,15,20-tetra(4- pyridyl)-21*H*,23*H*-porphine palladium(II). For initial investigations in this area the palladium porphyrin was chosen because I wished to ensure that the metal at the porphyrin centre would not interfere in the coordination chemistry involved in assembling the network. In 1990 I obtained solvated $\{CuI\ [Pd(tpp)]\}BF_4$ in the form of crystals too small for a full X-ray structural determination (with the technology of the day), but the unit cell was tetragonal as expected for a PtS-related structure and the cell dimensions agreed very closely with those estimated for the intended PtS-related network. Subsequently, using the more readily available Cu^{II}(tpp) as the square planar component together with Cu^I or Ag^I as the tetrahedral nodes, we obtained much larger crystals which had almost exactly the intended structure (Figure 5).[14] The channels in the structure, filled with highly disordered solvent and anions, were very spacious, the framework occupying less than half the volume of the crystal.

We were also able to obtain PtS-related networks using, for the role of square planar node, the more extended building block 5,10,15,20-tetrakis(4-cyanophenyl)-21H,23H-porphine, tcpp, (Figure 6).[14] In this case a second, identical but independent network interpenetrated the first and *vice versa.*[14] Evidently the porphyrin units from the two separate networks were significantly attracted to each other forming intimate pairs so that the two separate 3D networks hugged each other closely throughout their length as can be seen in Figure 6b. Spacious channels accounting for ~70 % of the volume of the crystal were thereby left within the doubled-up 3D network (Figure 6b).

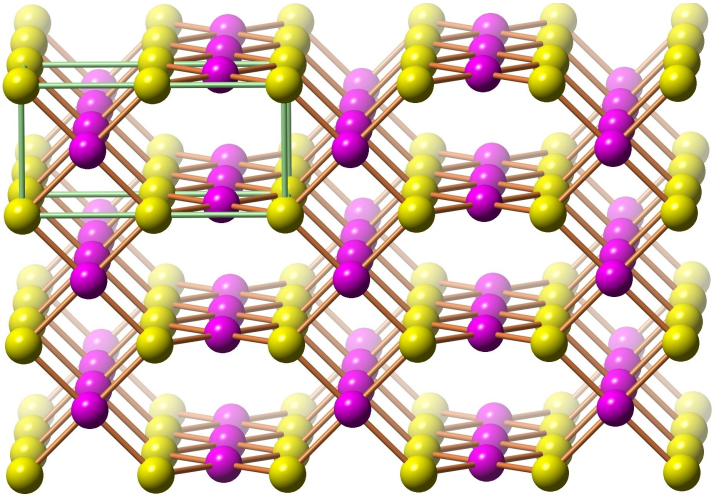


Figure 3. The parent PtS net (Pt purple, S yellow).

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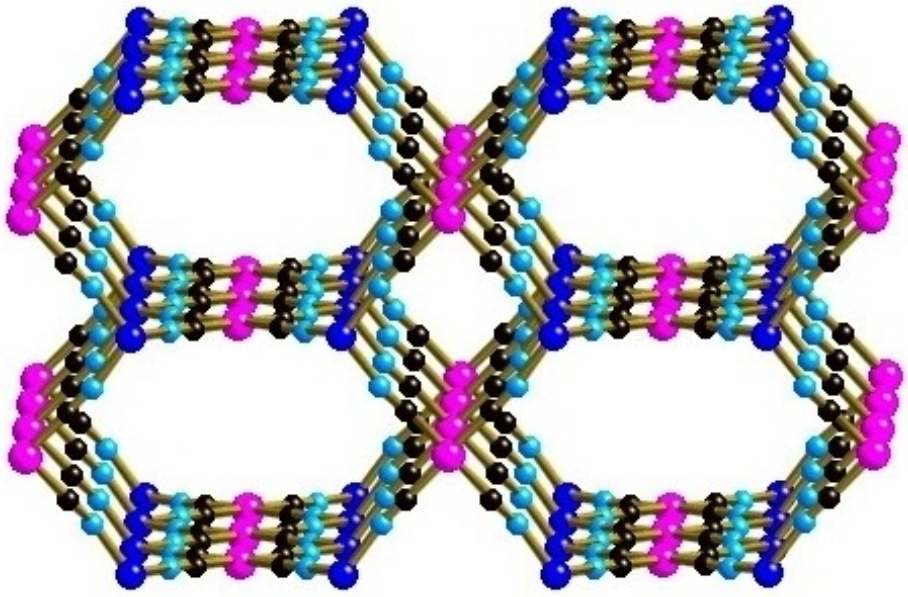


Figure 4. The PtS-like $\{Cu^{I}[Pt(CN)_4]\}^{-}$ framework.

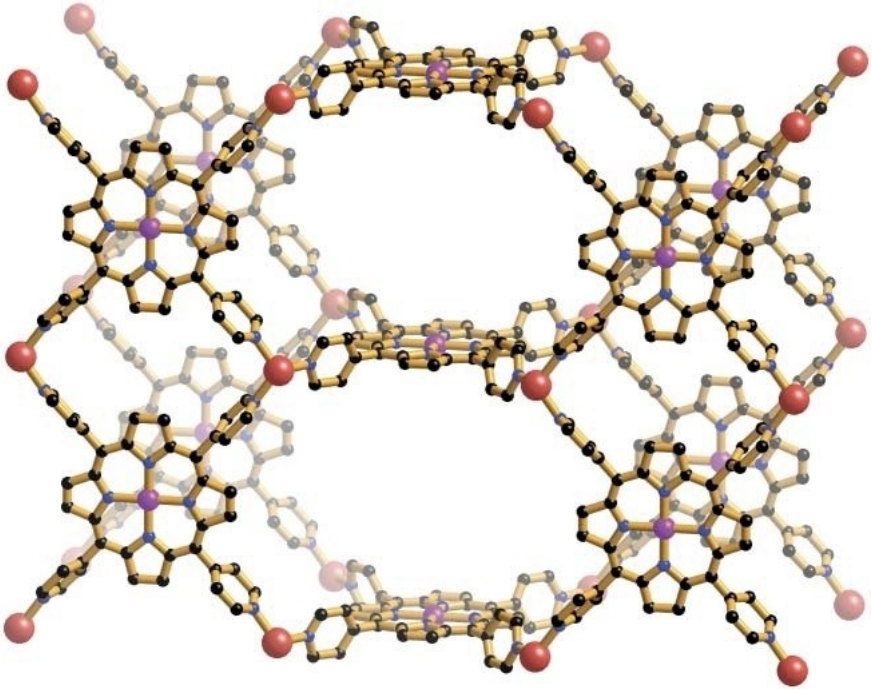


Figure 5. The PtS-like $[Cu^{I}(Cu^{II}tpp)]^{+}$ framework.

The boracite-related net (Figure 7) is one of the simplest and most symmetrical of a number of possible nets consisting of trigonal nodes and tetrahedral nodes, each trigonal node being connected to three tetrahedral nodes, and each tetrahedral node being connected to four trigonal nodes. The ligand tripyridyltriazine, tpt, (see Figure 8a for tpt structure), is predisposed to bind three metal centres at the corners of an equilateral triangle. In 1996 we reported that the reaction of

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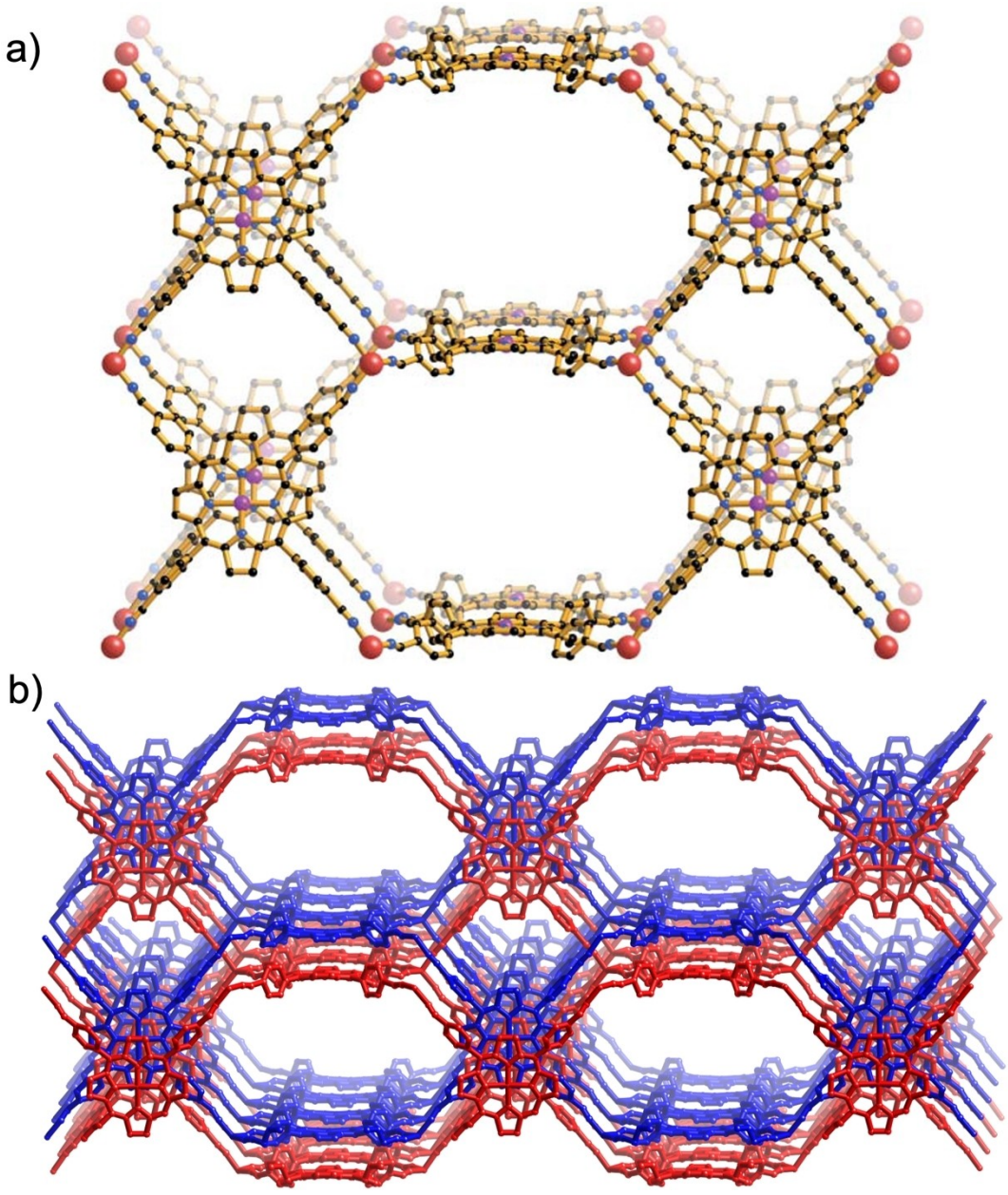


Figure 6. a) A single PtS-like $[Cu^{I}(Cu^{II}tcpp)]^{+}$ framework b) two interpenetrating $[Cu^{I}(Cu^{II}tcpp)]^{+}$ frameworks making close contact, thus leaving large channels accounting for ~70% of the volume of the crystal.

tpt with $Cu^{I}ClO_4$ produced crystals with cubic symmetry of composition $Cu(tpt)_{4/3}(ClO_4)$.solvate.[15] The structure consisted of two independent interpenetrating networks, both with the topology of the boracite net. Eight "cage-like" units can be seen in the representation of the parent boracite net in Figure 7; an analogous cage in the structure of the $[Cu(tpt)_{4/3}]^{+}$ network is shown in Figure 8a. For clarity in the representation of the extended $[Cu(tpt)_{4/3}]^{+}$ network, a simplified form of these cages is to be used; a single simplified cage is shown in Figure 8b and eight of these irepresenting the extended network are shown in Figure 8c, in which the boracite-like topology can be clearly seen. $Cu(tpt)_{4/3}(ClO_4)$ was one of several examples of interpentration that we discovered in the early 90's and in 1998 we published a review of interpenetration.[16]

We realized that when three bidentate ligands are coordinated to an octahedral metal centre the metal itself becomes a planar trigonal node and that this might give us

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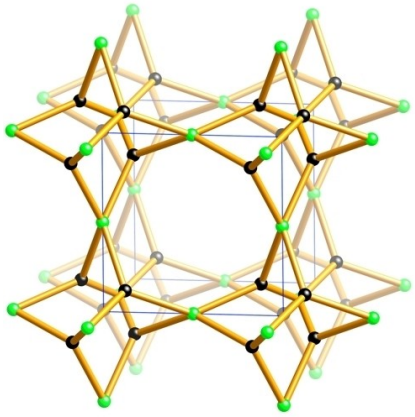


Figure 7. The cubic boracite-related net.

access to a wide range of unexplored 3-connected coordination networks. In particular, of all the possible 3D 3-connected nets, the cubic and chiral (10,3)-*a* net, seen in Figure 9, is the simplest, the most symmetrical and (other things being equal) the most "open". Wells considers that, amongst the many possible 3D nets, (10,3)-*a* "occupies a unique position";[12] it appeared to us in our early network building endeavours to be a very worthy target. The ligand hexaazatriphenylene, hat, (see Figure 10a for hat structure) is pre-organized to chelate three metal centres at the corners of an equilateral triangle and has the potential to act as a planar 3-connecting node in a coordination polymer. We reported in 1998 that hat, upon reaction with either $AgClO_4$ or $AgBF_4$ in nitromethane, gave crystals of composition $Ag(hat)X.2CH_3NO_2$ ($X{=}ClO_4$ or BF_4) which did have the (10,3)-*a* topology.[17] Every hat component was attached to three Ag^+ centres at the corners of an equilateral triangle and every Ag^+ centre was chelated by three hat ligands whose centres were located at the corners of an equilateral triangle (Figure 10a). All the metal centres had the same absolute configuration, generating the chiral (10,3)-*a* network seen in Figure 10b.

The viability of our net-based, pre-organized building block approach to framework construction was thus firmly established by the late 90's. A mere glance at the pictorial representation of, for example, the PtS-related structure, as seen in Figure 5, with its spacious channels giving access to banks of large, face-on, potentially catalytically active porphyrin units would have been sufficient for any chemist by 1994, to see immediately the enormous potential provided by the net-based, pre-organized building block approach. It was very clear to us at that stage that vastly more opportunities for new chemistry were on offer here than we could possibly explore and exploit ourselves. This 1994 PtS paper effectively constituted an invitation to as many others as might be interested, to generate an essentially unlimited range of coordination network structures in the future, paving the way for the subsequent explosion in reports of such networks.

The principles underlying the successful pre-organized building block approach to network construction were presented in structure-based terms in 1990,[6] and 1992,[9] and in net-based terms in 1994,[14] 1996,[8] and 1998.[16]

2.3. Pre-Organized Carboxylate-Based Building Blocks

In 1995 the first coordination polymer to be called a MOF was reported, namely $Cu(4,4'\text{-bipyridine})_{1.5}(NO_3).1.5H_2O$.[18] The bonds holding this polymer together were Cu–N bonds, like those used in our earlier exploratory network-building studies. Consideration is given below to the uniqueness of MOFs; we note at this point that the first ever MOF was ordinary. This research group subsequently greatly extended our net-based, pre-organized building block approach, generating very large numbers of new, extremely beautiful coordination polymers in which the pre-organized ligands carried carboxylate donors. These materials exhibited permanent porosity promising useful real-world applications such as gas sorption. By the early 2000's the metal-carboxylate-based coordination polymers were being presented as a unique class.[19] Emphasis was now placed on the strength of the metal-carboxylate bonds in these systems, alledgedly differentiating them completely from networks previously constructed by deliberate design that were held together by metal-ligand bonds judged to be "weak". Whilst $Cu(4,4'\text{-bipyridine})_{1.5}(NO_3)$ qualified as a MOF in 1995,[18] by the early 2000s, the "weak" Cu–N bonds by which it was bound together would exclude it from this, by now, unique class. Likewise, all the designed, pre-organized networks with "weak" Cu–N bonds that had been reported earlier were set aside, together with – most importantly - *the ideas underlying their design and construction.* Large and rapidly increasing numbers of workers in the field were unaware of the fact that the deliberate assembly of designed building blocks to give planned polymeric structures had been extensively explored prior to the advent of MOFs.

With relation to the superior robustness of the metal-carboxylate-bound coordination polymers compared with the earlier Cu–N bound examples, the latter were not designed to provide materials immediately solving major problems; rather, they were intended to demonstrate, in as simple a way as possible, how the net-based, pre-organized building block approach might provide the basis for the future production of essentially unlimited numbers of solid materials with targeted topologies and structures and, possibly, with useful properties.

The following considerations demonstrate that MOFs are simply one type of coordination polymer, not a unique class. Large numbers of neutral and anionic species act as ligands providing dative bonds to metal centres, whereby a huge array

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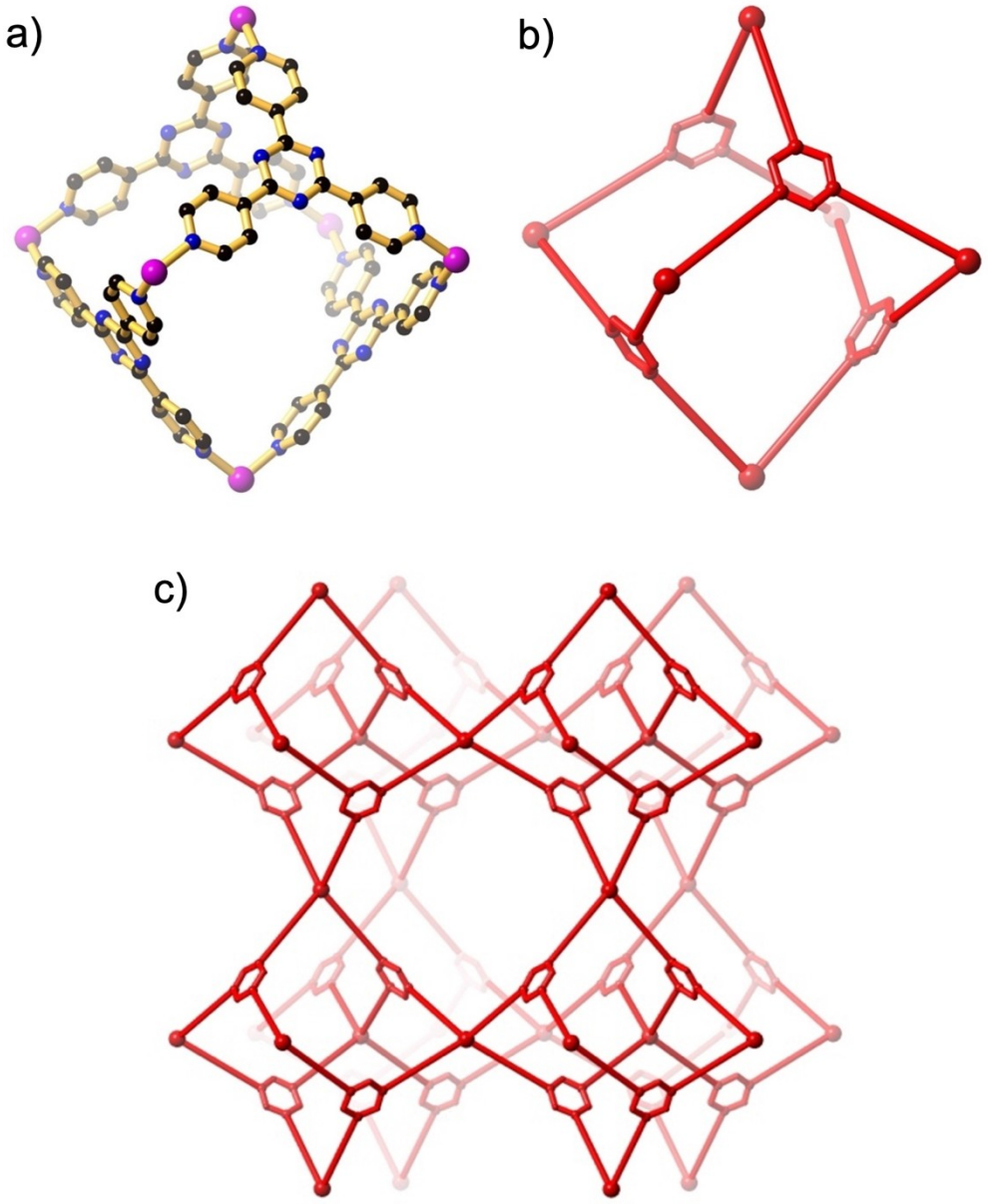


Figure 8. a). A single "cage component" in the structure of the $[Cu(tpt)_{4/3}]^+$ network (compare with Figure 7), b) simplified version of one of the cages in the $[Cu(tpt)_{4/3}]^+$ network (compare with Figure 8a). The hexagonal rings represent the triazine components of the tpt, c) eight simplified cages representing the extended boracite-like structure of the $[Cu(tpt)_{4/3}]^+$ network.

of discrete coordination complexes is generated; carboxylates are just one donor type amongst many within this extensive collection of ligands. Discrete coordination complexes vary widely in stability, depending amongst other factors on the donor ligands. It is no surprise therefore that coordination polymers, held together by the same ligand-to-metal coordinative interactions as those operating in the discrete complexes, also vary in stability – it would be amazing if they did not. The fact that the carboxylate-based coordination polymers are more robust than their Cu–N-based conceptual predecessors is not a persuasive reason for assigning them unique status; they are just one type of coordination polymer.

In 2003, in a very highly cited Nature article entitled "Reticular Synthesis and the Design of New Materials" framework construction is given the name reticular synthesis.[19] One of the central concepts considered in this article, putatively differentiating reticular synthesis from

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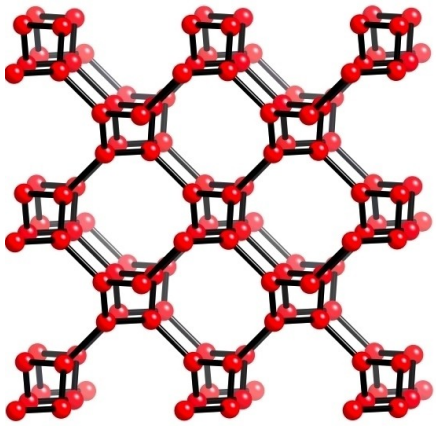


Figure 9. The cubic and chiral (10,3)-*a* net, seen here in its most symmetrical configuration.

previous approaches to network construction is that of secondary building units (SBUs). The authors write:

"*The design principles for MOF-5 will be discussed here to show that SBUs have intrinsic geometric properties that facilitate network design and help us to address the issues of network synthesis and robustness. In MOF-5 $Zn_4O(CO_2)$ units containing four ZnO_4 tetrahedra with a common vertex and six carboxylate C atoms that define an octahedral SBU are joined together by benzene links. This leads to a cubic network in which the vertices are the octahedral SBUs and the edges are the benzene struts.*".

The assembly, the structure and the connectivity of MOF-5 can in fact be readily appreciated in terms of simple geometry and basic ideas from coordination chemistry, without any recourse to considerations about SBUs. The long-known structures of basic beryllium and zinc acetates, $M_4O(CH_3CO_2)_6$, (M=Be or Zn) provide six acetate C–C bonds that are directed to the corners of an octahedron. If the acetate units are substituted by "linear" bridging dicarboxylates, such as terephthalate, it is easy to see that a cubic α-Po network will result. A figure is presented in the reticular synthesis article (Figure 2[19]) intended to clarify just what SBUs are. Molecular structures are shown in this figure representing several pre-organized poly-carboxylate building blocks - a trigonal 3-connecting ligand, a tetrahedral 4-connecting ligand, a planar 4-connecting ligand (a tetra-substituted porphyrin) and a 6-connecting ligand. It is clear, simply on the basis of the pre-organized structures of these ligands, how they are likely to act as building blocks in derived coordination polymers. It is not at all clear how the "SBU representations", accompanying each ligand in the figure, afford any insight beyond what is already conveyed by the molecular structures. Researchers are free to use whatever concepts they find helpful, but SBUs appear (to the author of this account at least) to provide little insight and are quite definitely not of central, discriminating importance,

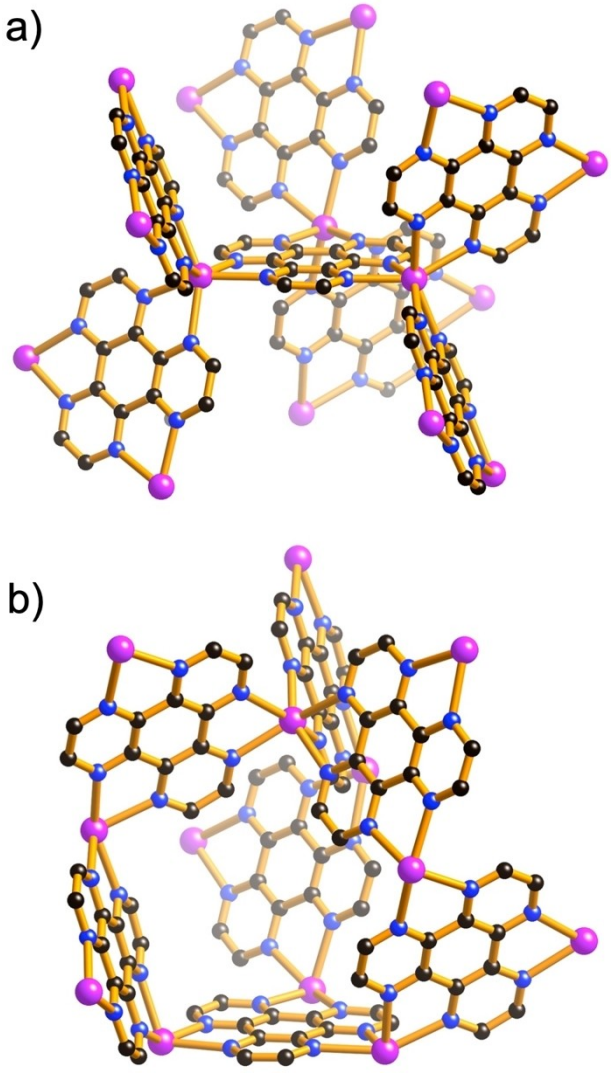


Figure 10. a) Part of the $Ag(hat)^+$ network showing that every hat ligand binds three Ag^+ centres and every Ag^+ is chelated by three hat ligands, b) part of the $Ag(hat)^+$ network showing the 10-gons of trigonal nodes that are one feature of the (10,3)-*a* topology.

setting SBU-based approaches completely apart from all others.

In 1990 we proposed that ligands that provide chelating sites for metal binding might (in future exploration) afford significantly more robust framework structures.[6] With relation to making use of chelation to enhance stability, the authors of the reticular synthesis article write "We have focused on using the carboxylate functionality to *chelate* metal ions and lock them into rigid and thus directional metal-oxygen-carbon clusters".[19] The carboxylate donors in MOF-5 are in fact acting as bridging ligands, not chelating ligands. If they were to act in a chelating manner, 4-membered MOCO rings would be generated, providing poor network stability.

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To summarize the conclusions reached in this examination of the features of reticular synthesis reputedly differentiating it from previous planned network building: 1) MOFs are just one type of coordination polymer, not a unique class and 2) The concept of SBUs provides little insight and is by no means essential in envisaging and constructing new coordination polymers/MOFs.

It is enlightening to compare the concepts underlying reticular synthesis with those underlying the net-based pre-organized building block approach which had been laid out in 1994 in the following terms:[14]

"*One approach to crystal engineering that we have been developing is first to choose as a geometrical/topological model one of a number of simple 3D nets such as diamond (all centres tetrahedral), α-Po (all centres octahedral), PtS (equal numbers of square planar and tetrahedral centres), rutile (octahedral and trigonal centres in 1:2 proportions) and so on, and then try to devise ways of chemically linking together molecular building blocks with a functionality and a stereochemistry appropriate to the chosen net.*".

These concepts are to be contrasted with those presented in the reticular synthesis article in a section headed "Logic of Synthesis by Design" containing the following passage:

"*On the conceptual level, the underlying process for logical synthesis of MOFs starts with the designer choosing a specific target network, which is then deconstructed into its component geometric units. Molecular building blocks with the same geometry as those of the units are then assembled into a MOF structure that has the target network topology.*"

It is clear that the concepts underlying reticular synthesis are indistinguishable from those underlying the earlier net-based, pre-organized building block approach to framework construction, a fact unmentioned in the reticular synthesis paper.

3. Summary and Outlook

During the 90's the building block approach was employed by numerous researchers to construct not only coordination polymers but also hydrogen bonded networks.[20] Notable contributors to the remarkable growth in this area at that time were the groups (in no particular order) of S. Kitagawa, M. J. Zaworotko, O. M. Yaghi, J. D.Wuest, O. Ermer, I. D. Williams, M. J. Rosseinsky, M. D. Ward, X.-M. Chen, M. W. Hosseini, M. Schroder, G. Ciani, N. Champness, G. R. Desiraju, M. Fujita and D. Proserpio. The early exploratory work described in this article paved the way for the subsequent explosion of research activity in the CP/MOF area. There is every indication that the pre-organized, net-based, building block approach to the construction of targeted coordination polymers, whether or not referred to as the reticular synthesis, will be amenable to boundless future extension, improvement and refinement. As was foreshadowed in 1990,[6] the great variety of metal-ligand bond types and the associated enormous diversity in electronic structures and properties seen in discrete, non-polymeric coordination complexes and organometallic species can, in principle, be mimicked in coordination polymers, providing a still largely untapped area of exploration, potentially affording a huge range of new, designed solid materials, possibly with all sorts of useful properties.

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