

Dr. Stuart R Batten

Details of Selected Research Themes (as of mid 2006)

My research interests lie largely in the field of crystal engineering, and in particular, coordination polymers. This research aims to understand and then control the way molecules assemble and pack in the solid state. This is important as the packing arrangement often controls the chemical and physical properties of the resultant material.

Coordination polymers - design, synthesis and interpretation

I have a long history of significant contributions in this area. I was the first student in the group of Prof. Richard Robson at Melbourne to work on the crystal engineering of coordination polymers. This pioneering group is recognised as having led the way in this new and now greatly expanded area of research, especially in reporting most of the earliest work and establishing many of the basic principles and techniques in the area. Publication 2 (112 citations), for example, was highlighted in an editorial article in *Science*, and chosen as one of the highlights of the year for chemistry in the *Encyclopaedia Britannica, Book of the Year*, 1996.

This research interest has continued through various postdoctoral positions to the current day. We are interested in the synthesis, structure and properties of these new materials. With Prof. Keith Murray (Monash), we regularly test the magnetic properties. With Dr. Alan Chaffee we have recently begun to test their gas sorption properties, particularly for CO₂; we have already found one very promising material which we are studying further for possible application to pollution control. Many of the more recent research themes listed below fit into this general overall area, and my expertise and standing has been recognised by invitations to review this area or contribute to journal special issues on the subject (publications 30, 35, 46, 61, 67, 68, 79, 87, 95, B5). I have also been invited by the Royal Society of Chemistry to write a Research Monograph on the topic (in progress). **Publications** B1, B5, 1, 2, 3, 4, 5, 7, 12, 17, 21, 23, 29, 35, 46, 47, 57, 79, 87; **Grants** F29804208, F00103375, DP0208486, DP0449718, DP0771940.

Structural and magnetic properties of transition metal pseudohalides

I initiated this work in 1996 while working in the group of Prof. Keith Murray at Monash. We were subsequently the first to report the landmark M(dca)₂ (dca = dicyanamide, N(CN)₂⁻) series of new molecule-based magnets (publication 15; 225 citations). Since this initial publication dca has become a 'hot' ligand in the area of molecular magnetism. Intense interest and competition has resulted from a number of groups around the world, with more than 250 publications on this ligand appearing since. Following the initial study of the binary metal dicyanamide complexes, we investigated the modification of network topologies through the introduction of bridging and terminal coligands. Much of this work was undertaken in the period 2000-2005. After determining the crystal structures and magnetic properties of over 100 dca containing coordination polymers we have concluded that the bridging mode of the dca ligand is very important – i.e. the rare $\mu_{1,3,5}$ bridging mode is usually necessary for the occurrence of long-range magnetic ordering. The metal-dca system was also found to be very malleable; subtle changes in coligands can lead to dramatic changes in structure.

Another indication of the malleability of this system was seen in the structures of anionic M(dca)₃⁻ and M(dca)₄²⁻ networks. We found that the nature of the counter cations required to balance charge has a dominant structure-directing role. That is, the network topology is templated by the cation; a large variety of networks with different topologies have been discovered through the simple variation of cations.

Prof. Murray and I continue to collaborate on this work, and we have extended this research to examine other closely related pseudohalide ligands. We summarized our work to date (and that of others) in a 2003 review (publication 61; 149 citations). This work has formed parts of successful ARC APD and ARF Fellowship (Batten) and Small, Large and Discovery Grant (Murray, Batten/Turner) applications, and has formed the basis of six completed Honours projects and one current and four completed Ph.D.

projects at Monash alone. **Publications** 15, 19, 20, 22, 24, 25, 27, 28, 30, 33, 34, 36, 37, 41, 46, 48, 51, 52, 54, 56, 60, 61, 67, 68, 70, 72, 88, 97, 111; **Grants** F29804208, F00103375, AINGRA05007.

Heterobimetallic Coordination Complexes Containing Rare Earth and d-Block Ions 2006-present

This research aims to study the synthesis and structure of new coordination complexes and polymers which contain both lanthanoid and transition metals in the same complex. Initial work has focussed on pseudohalide ligands such as dca and tcm, as well as the related $C(CN)_2NO^-$ and $C(CN)_2NO_2^-$ ligands. These last two ligands have been particularly interesting, and we have synthesised a number of new complexes and coordination polymers of these ligands with transition metals and/or lanthanoids. We have also found that these ligands readily undergo decomposition reactions in which water or alcohols are added across one of the nitrile groups; this decomposition leads to a new series of ligands which have also provided interesting new compounds. **Publication** 95, 111; **Grant** DP0665938.

Chemically active coordination polymers and metallosupramolecules

This research aims to design new coordination polymers and metallosupramolecules which, unlike the majority of existing systems, are deliberately engineered to contain chemically active sites in the final assembly. Initial work concentrated on obtaining (successfully) 'proof of concept' for our design strategy. Notable results include a nanometre sized molecular ball containing 8 ligands and 14 metal ions; the inside surfaces of these 'nanoballs' are decorated with potential ligand binding sites, and the crystals show significant hydrogen storage properties; **we will shortly submit this work to *Nature***. In a series of crown ether based structures we have been able to control the ligand binding length by inserting different cations into the crown (resulting in up to a twofold variation in ligand length). This is a completely new phenomenon, unreported in the literature, and we are seeking to exploit this to generate a new class of materials with cation-controlled porosity. We are testing other properties of these new materials, including gas sorption (with Alan Chaffee and Cameron Kepert), and catalytic activity (several Cu-containing materials have been shown to catalyse dehydrogenation reactions). **Publications** 77, 91, 99, 100, 104; **Grants** DP0449718, DP0771940.

Interpenetration

I am one of the world's leading experts on the phenomenon of interpenetrating networks in crystal structures. In the design of network structures an understanding of interpenetration is vital to the analysis and design of new structures. One must understand not just the topology of the individual networks formed, but also the *topology of interpenetration*. Publication 14 (1998; with Richard Robson; 1684 citations) was the first comprehensive review on this subject, and involved not only a review of the literature, but in many cases re-interpretation of structures, including a number that were incorrectly described in the original literature. It is one of the most cited papers in crystal engineering. It also outlined and introduced, for the first time, a systematic method and nomenclature for the description interpenetration topology. We also subsequently introduced and defined the description "self-penetration" for infinite networks which have knot-like topology (publication B2; 1999). This culminated in 2001 with a sole author publication which extended the interpenetration nomenclature further, making it both more general and more detailed (publication 42). **The nomenclature we developed has now been widely adopted in the literature**. Furthermore, this paper was the very first 'Highlight' paper written for the Royal Society of Chemistry journal *CrystEngComm*, and is the **most highly cited paper published in this journal** to date (188 citations). I have also set up a web site listing all known examples of interpenetration, which is a regularly updated resource used by chemists around the world (www.chem.monash.edu.au/staff/sbatten/interpen/index.html). Networks are classified according to the above nomenclature. The web site has been cited in the literature several times (and has received almost 5000 'hits'). Papers B2, B3, B4, 14 and 42 were as a result of invitations to write on this subject. **Publications** B2, B3, B4, 14, 26, 28, 30, 42, 62, 71.

Structural description and topology

I also have a widely recognised expertise in the analysis of the topology of network solids. This involves reducing a crystal structure to a network of nodes and links, then recognising and describing that network in order to both understand and describe the overall crystal structure. This understanding can then lead to improvements in crystal design. This expertise has resulted in numerous requests for my advice and opinion on unusual crystal structures from around the world, and in particular from several Chinese groups. For example, in one especially significant structure I recognised that the

underlying network topology was a new example of a *uniform net* (publication 62). Uniform nets are a particularly fundamental class of networks in which all the shortest circuits are of the same size. An even more special subset of these are the Platonic uniform nets, in which all the nodes are of the same connectivity. The topology of the structure was found to be a *new* Platonic uniform net. Not only was this the first real, chemical example of this network, but the net had in fact been unrecognised in the leading network texts (one text goes as far as saying “We are not aware of the existence of a 4-connected net in which there is a square coplanar arrangement of links at each point and for which the point symbol is n^6 ”). Thus it was also the first uniform net to contain only planar four-coordinate nodes, and the first four-coordinate uniform net not to be described by the Schläfli symbol 6^6 (it is 8^6). **Publications** 11, 14, 16, 42, 53, 62, 63, 65, 69, 71, 73-6, 78, 80, 81, 85, 86, 89, 93, 94, 96, 98, 103, 106, 108, 109, 112.

Ionic liquids

This is a collaboration with the MacFarlane group at Monash, and involves the synthesis and characterisation of new ionic liquids with a range of polynitrile pseudohalide anions. Following the success of the dicyanamide anion, I suggested that the tricyanomethanide anion be investigated. This led to the first series of ionic liquids to contain this anion. They were found to have similar conductivity, thermal stability and electrochemical stability to the dca ionic liquids, but are not as hygroscopic. Furthermore, their use in dye-sensitized solar cells has been investigated; of the three anions tested, tcm had the lowest viscosity and the best conversion efficiency. We are now currently investigating the use of other similar but unexplored pseudohalide anions. **Publications** 64, 92.