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The inorganic chemistry of solids: where have we come from? Where are we going?

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Examples of work published recently in *Dalton Transactions* are used to illustrate some emerging themes and trends in the inorganic chemistry of solids at the turn of the millennium. Among the topics surveyed are the synthesis of new classical solids, especially by low temperature methods; organic–inorganic composite lattices, including inclusion compounds; supramolecular organisation and directed synthesis, and new molecular compounds with unusual collective electronic properties, such as superconductivity and magnetism.

Introduction

'State of the Union' speeches are annual events in the American political calendar. The founding fathers of that country clearly felt that once a year was a suitable interval to take stock, survey the horizon both back and forward and assess what problems had successfully been tackled, difficulties overcome, and what was still left to be done. In science we are not given so much to this style of reflection, but it remains a useful discipline to ask ourselves from time to time where we have come from and where we are going. Once every millennium, though, is a pretty tall order!

Chemistry had its roots in technology (a salutary thought as we grapple with government Foresight initiatives), through processes that were honed empirically throughout millennia before any serious thought was devoted to the underlying principles governing the behaviour of matter. A recent article in *Dalton Transactions* makes this point very nicely in relation to the extraction of silver in medieval Latin America. In fact, as far as solid state chemistry is concerned, the principal areas of interest at the turn of the last millennium would have been the extraction of metals from their ores by various forms of reduction, and the manufacture of ceramics, both the objects themselves and the glazes and colours that coated them. Apart from mechanical properties and colour, the physical behaviour of solids was not of any interest until the nineteenth century. However, nowadays it constitutes as large a field of study as the chemical, even taking into account the ubiquitous presence of catalysis.

What is solid state inorganic chemistry?

Before describing (let alone trying to sum up) the 'state of the union' at the turn of the second millennium as far as solid state inorganic chemistry is concerned, it must be worth considering

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for a moment what the aims of the subject are at this moment in its evolution. First and foremost must be, as always since the birth of our discipline in the nineteenth century, to go on probing what kinds of compounds are capable of existing, and how they correlate with the position of the constituent elements in the Periodic Table, which will always remain the palette that chemistry paints from. New and unexpected kinds of compound continue to flow from synthetic laboratories in just as great a profusion as they ever did, especially as the range of preparation methods continues to widen: 'soft' chemistry, solvothermal methods, self-sustaining reaction, are all playing their part.

Having got their hands on a new solid, the next question that chemists want to answer is: what is the arrangement of the constituent atoms and how does it relate to the Periodic Table? Here, too, the methods open to determine crystal structures grow ever more powerful, from atomic resolution lattice imaging electron microscopy and synchrotron-based EXAFS for local structure determination to third generation neutron powder diffractometers like GEM at the ISIS pulsed source,[1] for small samples and rapid data collection. The final question concerns properties and how they, too, relate to the electronic structures of the elements concerned. Here, solid state inorganic chemistry is overlapping with the new and burgeoning field called materials chemistry,[2] especially as the properties being called into question are electronic and, in particular, collective, *i.e.* pertaining to the aggregate, such as magnetism or superconductivity. If that sounds dangerously like physics to chemical ears, there is certainly no lack of chemical properties for us to attend to, principal among which are the reactions of molecules inside, or on the surface of, solids. If in addition such reactions are catalytic, then technological interest is immediately raised.

Providing chapter and verse for all the generalisations of the last few paragraphs would be daunting, and perhaps not relevant to the spirit of a millennium perspective. However, extracting current trends and new directions certainly is. The question is, how to do that in a small but readable compass. It seemed to me that, as one of the world's leading archival journals of inorganic chemistry, *Dalton Transactions* itself ought to be a showcase of these trends, and a glance through the last few months' issues confirms the hypothesis. What follows is therefore a personal view of developing themes in solid state inorganic chemistry at the time of the millennium, illustrated by examples taken from that journal.

New classical solids

If the wellspring of creativity in chemistry is in synthesizing new compounds (that is, combinations of elements that have never been seen before), then it is easier to imagine how that might be done if we allow that the structures and stoichiometries become ever more complicated. Synthesizing simple combinations, and new examples of classical structure types, sounds altogether more difficult and challenging. The advent of low temperature synthesis (espoused in particular by Jean Rouxel and his colleagues,[3] and hence given the French name '*chimie douce*', or soft chemistry) has brought a new emphasis to this area over the last few years, but it is fascinating to see that even the more conventional high temperature methods continue to yield new phases of unusual kinds. Such methods remain common in the oxide field, but the chemistry of nitrides is still relatively uncharted territory, though potentially of great significance as a source of new superconductors. This is partly due to the difficult chemistry involved. Thus the new ternary nitride oxide $Sr_4[MoN_4]O$ was synthesized by treating strontium nitride with molybdenum nitride under a low partial pressure of oxygen in a stainless steel crucible, but to make the Sr_2N starting material one has to treat strontium metal dissolved in liquid Na with N_2 close to 1000 K.[4] It is fascinating to see that the Mo in this compound is tetrahedrally co-ordinated, in the form of isolated $[MoN_4]^{6-}$ units, while the oxide ions are exclusively within the co-ordination sphere of the Sr (Fig. 1).

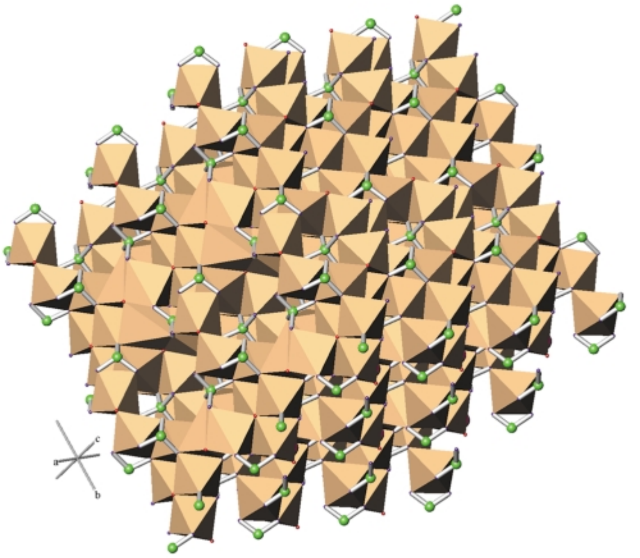

Fig. 1 The crystal structure of $Sr_4[MoN_4]O$ projected on to the [111] plane. Reproduced from ref. 4.

Doping transition metal ions into zeolite framework compounds has become a growth industry because, trapped in the unusual environment of a silicate or aluminophosphate host, they take on catalytic oxidation properties.[5] Consequently, increasing the transition metal up to the level of complete stoichiometric substitution is an important synthetic endeavour, and even some very simple compositions are found to crystallise in framework structures. A recent example is $CsCoPO_4$, with the ABW framework topology (Fig. 2), which was prepared simply by grinding together $(NH_4)_2HPO_4$, Cs_2CO_3 and $Co(NO_3)_2{\cdot}6H_2O$, firing at 1000 °C and cooling at a controlled rate.[6] The panoply of characterisation methods, such as EDAX (energy dispersive X-ray analysis), DTA and both X-ray and neutron powder diffraction, provide an object lesson in identifying such new solids.

Low temperature syntheses are not only providing new routes to familiar compounds, formerly only prepared by high temperature ceramic methods, but frequently lead to new compounds in which elements of familiar structures appear in new guises. Zintl compounds, formed from Group 1 and Group 15 elements, are among the long established classics of solid state chemistry,[7] but by treating aryl-phosphines and -arsines with $E(NMe_2)_3$ ($E = As$ or Sb) Zintl compounds containing E_7^{3-} emerge, though with cations such as $Li(TMEDA)^+$.[8]

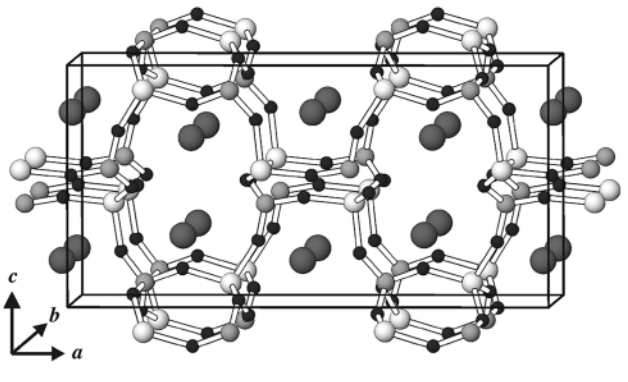

Fig. 2 The crystal structure of $CsCoPO_4$ projected close to the [010] plane. The small black spheres are O, large dark spheres Cs, light spheres Co and intermediate spheres P. Reproduced from ref. 6.

Organic–inorganic composite compounds

Combining organic molecular groups with inorganic ionic ones is a powerful method for introducing novel functionality into inorganic crystal lattices, as we pointed out in the specific instances of magnetic interactions and topotactic polymerisation some years ago.[9] The field continues to broaden and new examples are turning up with both transition-metal and post-transition-metal cations, the majority based on alternating layers of organic and inorganic material. Bonding between the layers may be ionic, covalent or donor–acceptor in type, and in addition the 'organic' component can also contain metal ions in the guise of molecular co-ordination or organometallic complexes.[10] A few recent instances illustrate the variety of structure types emerging.

Transition metal oxides in the form of infinite one- or two-dimensional anions remain quite rare when combined with organic molecular cations, so the presence of $[V_4O_{12}]_n^{4n-}$ chains in such a situation is of interest, especially so when one finds that the counter cation is a 1,2,4-triazolate (trz) complex $[Cu_3(trz)_2]_n^{4n+}$.[11] The latter trimeric units are further linked together into undulating sheets (Fig. 3), which give the compound quite complicated magnetic properties. It is also clear that the conventional 'ship in a bottle' approach to rationalising the arrangement of the metal–organic units within an oxide framework, as often involved in framework compounds, is not adequate to describe the supramolecular organisation here, as the vanadate chains lie side by side between the copper–triazole layers. Interaction (called synergistic by the authors) between the organic and inorganic components is clearly an important factor.

Although the 'synergy' between molecular metal–organic and infinite chain inorganic parts of the vanadate salt arises from the shapes of the components, the major interactions between them are clearly coulombic. In the large, and still growing, family of organophosphonate salts co-ordination of the PO_3 groups to the metal ion is the main factor determining the lattice structure. Many of the phosphonates are transition metal compounds, most famously the zirconium(IV) series, though metal(II) examples from the 3d block furnish interesting examples of two-dimensional co-operative magnetism.[12] However, post transition metal elements, too, form phosphonate salts, as a recent example of a lead(II) compound indicates.[13] In contrast to the d-block phosphonates, the metal co-ordination in the B-subgroup examples is both irregular and variable, in line with their behaviour in many other simpler compounds: in lead(II) carboxyethylphosphonate there are three distinct metal sites with 3-, 4- and 5-fold oxygen co-ordination. Interestingly, each one can be thought of as derived from an $(N + 1)$-gon, with one vertex unoccupied, *e.g.* the 3-fold site from a tetrahedron, the 4-fold from a trigonal bipyramid and the 5-fold from an octahedron, thus revealing quite clearly the stereochemical role of the 'inert pair' of lead(II) electrons. Further complicating the structure is the bifunctional nature of the phosphonate, since the carboxylate O binds to metal as well as the PO_3.

An alternative mode of combining organic molecular with inorganic continuous lattice material in the solid state is, of course, by simple intercalation, but a variant of that process which has become increasingly used over the last few years is to employ organic molecules as templates around which an inorganic framework can be made to crystallise. Starting from alkylamines or quaternary ammonium salts, more and more elaborate molecules are being used now in an effort to encourage the formation of framework structures with larger cavities. A natural extension in this direction is towards macrocycles, such as 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane which, when added to the hydrothermal synthesis mix of magnesium acetate, $Al(OH)_3$, H_3PO_4 and water results in the formation of a completely new magnesioaluminophosphate, whose structure consists of remarkably large cages (approximately 9 by 10 Å)[14] (Fig. 4). However, in contrast to those of comparable size in the well known zeolites A, Rho and ZK-5, theses cages are only connected along one axis. Judicious choice of even more elaborate macrocycles will surely lead to further frameworks with pores tailored as to size and connectivity.

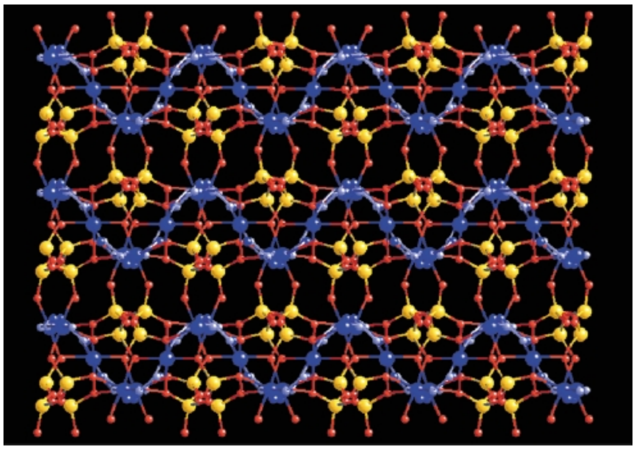

Fig. 3 The crystal structure of $[Cu_3(trz)_2][V_4O_{12}]$ projected on to the [001] plane. Reproduced from ref. 11.

Supramolecular lattices and directed assembly

In retrospect it is perhaps surprising that for so long co-ordination and organometallic chemists focussed their attention almost entirely on the synthesis and properties of isolated molecules, even though they relied on crystal structure determinations from crystalline solids for their knowledge of what they had made. The last two sections have demonstrated quite clearly how important intermolecular interactions are in determining crystal packing, but it is particularly in the area of co-ordination complexes that the directed synthesis of molecules for their packing properties has become dignified under the generic title 'supramolecular chemistry'. Multidentate ligands, locked into pre-ordained arrangements by co-ordination to metal ions having strong stereochemical preferences, furnish reliably predictable building blocks for constructing novel lattice topologies. Especially this is so when, in isolation, the ligands are ambidentate and so direct the formation of ordered infinite arrays of metal ions. A neat example from the pages of this Journal is the flexible tetradentate ligand 1,6-bis(4′-pyridyl)-2,5-diazahexane (BPDH), which readily forms crystalline compounds with Cu^I and Ag^I.[15] All such compounds contain infinite networks, but especially noteworthy is the fact that the dimensionality of the array changes with the shape of counter anion (tetrahedral or planar trigonal). Thus $Ag(BPDH)NO_3$ contains chains, while $Ag(BPDH)ClO_4{\cdot}CH_3CN$ and $Cu(BPDH)ClO_4$ both contain layers of infinitely connected cations, though with different

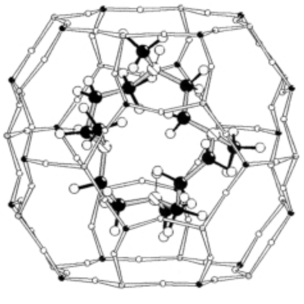

Fig. 4 Computer-simulated minimum energy configuration of diprotonated 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane within the cage of the magnesioaluminophosphate STA6. Reproduced from ref. 14.

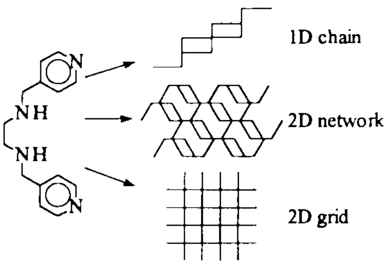

Fig. 5 Schematic representation of the infinite lattices formed by co-ordinating BPDH (see text) with Cu^I and Ag^I and NO_3 and ClO_4.

connectivities (Fig. 5). The crucial feature appears to be the anion, which forms N–H · · · O and C–H · · · O hydrogen bonds but with different arrangements depending on the number of O atoms.

When the ambidentate and polydentate ligands are also chiral, yet a further vista for constructing unusual polymeric lattices opens up, this time because the synthesis, being stereoselective, results in macroscopically chiral aggregates[16] (Fig. 6). What novel collective properties this may give rise to (physical, as in circularly polarised luminescence, or chemical, as in chiral recognition by adsorption in channels within the structure) remains very much to be seen. Neither are infinite helical chains confined to pyridine and bipyridine-containing ligands and the (now almost traditional) copper(I) and silver(I) centres: the triethylstannyltetrazole which forms the product of cycloaddition of Et_3SnN_3 and 4-cyanopyridine surprisingly also crystallises as a one-dimensional helical polymer.[17] In this case the "pitch" of the helix (Fig. 7) is very long (40 Å) because the pyridyltetrazole moiety is nearly linear, but evidently by ringing the changes one could imagine controlling this feature of the structure.

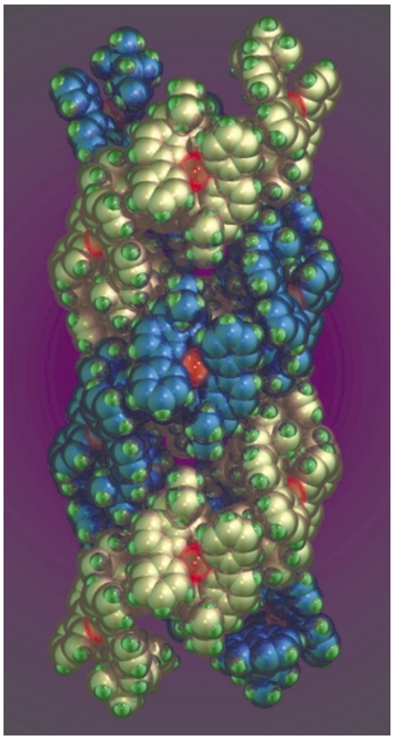

Fig. 6 Polymeric double helix in Ag[chirality-substituted BPDH]. Reproduced from ref. 16.

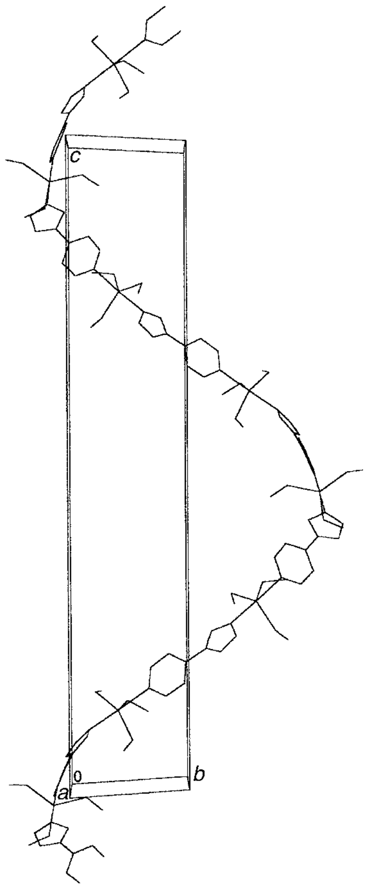

Fig. 7 The helical structure of 4-[2-(triethylstannyl)tetrazol-5-yl]-pyridine. Reproduced from ref. 17.

Molecular-based magnetic and conducting salts

Some 25 years have passed since the first highly conducting molecular materials were synthesized and subjected to full physical characterisation, and 15–20 since the first long-range ordered magnetic solids made from molecular components came on the scene. The first molecular metals were really organic, like doped polyacetylene and TTF–TCNQ, but molecular co-ordination complexes also appeared, the most famous being Krogmann's Salt, $K_2Pt(CN)_4Br_{0.30}\cdot 3H_2O$ (KCP). Most molecular superconductors are charge transfer salts of organochalcogen donors, first with simple inorganic anions like I_3^- and ClO_4 but subsequently with metal-containing species like $Cu(NCS)_2^-$. Recently interest has been turning towards designing molecular lattices in which superconductivity and long range magnetic order are combined,[18] but although this search has turned up many fascinating new compounds, this goal is yet to be fulfilled. It is important from a physical point of view because theoretical considerations suggest that these two properties should be inimical to one another. By making new compounds, the synthetic inorganic chemist's job is to see whether this is in fact true.

Current efforts to make magnetic superconductors from molecular components hinge on charge transfer salts with paramagnetic metal complexes as the anions. Out of such a strategy came the first paramagnetic molecular superconductor (and, incidentally, at the time the first superconductor of any kind containing a stoichiometric concentration of paramagnetic 3d ions).[19] However, predicting structures of such complex lattices is still not possible (though simulations of known structures have been successful[20]) and, as ever, synthesis springs surprises. Thus among the oxalato iron(III) salts of TFF and TMTFF (tetramethyl-tetrathiafulvalene) are compounds containing not only stacks of radical cations but binuclear oxalate-bridged $[Fe_2(C_2O_4)_5]^{4-}$ (Fig. 8), a previously unknown species that holds its own interest as a model of antiferromagnetic interaction between two high spin $3d^5$ ions.[21] The compounds themselves, however, are semi- rather than super-conducting.

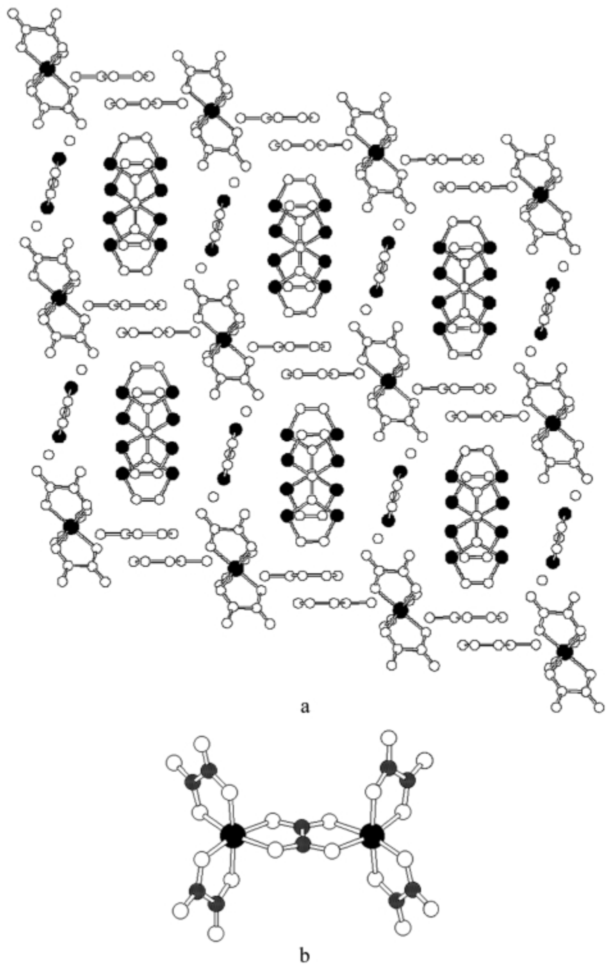

Fig. 8 The crystal structure of (a) $[TTF]_5[Fe_2(ox)_5]{\cdot}2C_6H_5Me{\cdot}2H_2O$ projected on the [010] plane, (b) the anion $[Fe_2(ox)_5]^{4-}$. Reproduced from ref. 21.

An alternative way to make molecular magnetic conductors is to assemble infinite purely inorganic structures interleaved with paramagnetic metal complexes, a variant on the organic–inorganic combinations referred to earlier. Again, chalcogenides form such extended structures, and might be expected to provide a fruitful hunting ground for new lattice types, while at the same time being possible conductors. A remarkable recent instance of this type is $\{[La(DMAC)_5(H_2O)_3(DMAC)_4]{\cdot}[W_3Ag_3S_{12}]\}_n$ where DMAC is *N*,*N*-dimethylacetamide.[22] The La (which almost certainly could be replaced by other 4f ions) is co-ordinated by five DMAC and three H_2O and the W_3Ag_3 units form rings. What is entirely unlooked for, though, is that both the cation and anion arrays form helices, the latter being shown in Fig. 9. The compound behaves as a semiconductor but it remains to be seen whether the bulk physical properties are influenced by the helicity.

Using molecular complexes (what the late Olivier Kahn,[23] one of the great proponents of the field called 'bricks') to construct lattices supporting long range magnetic order has been a strong growth point for inorganic chemistry over recent years, and seems likely to remain so, especially as technological outlets for some of the new chemistry are beginning to emerge. Unlike the compounds just referred to earlier in this section, the vast majority of so-called 'molecular based magnets' are electrical insulators, being in essence co-ordination complexes suitably organised in the solid state to facilitate superexchange interactions between moments largely localised on the d- or f-block metal ions. Given the enormous number of magnetic materials already known and commercially exploited, from the historic lodestone to the latest high coercivity Nd–Fe–B compounds, it is a legitimate question why chemists should spend much effort making a lot more.[24] Several answers can be given. First, molecular compounds are usually made at or near room temperature from solution, a far cry from high temperature ceramic or metallurgical methods: one could contemplate soluble magnets! Secondly, because they are insulators, they are often transparent, leading to many unusual optical effects. Finally and, in the context of basic inorganic chemistry, most important, they furnish new lattice architectures and properties, as recent work on cyano-compounds shows.

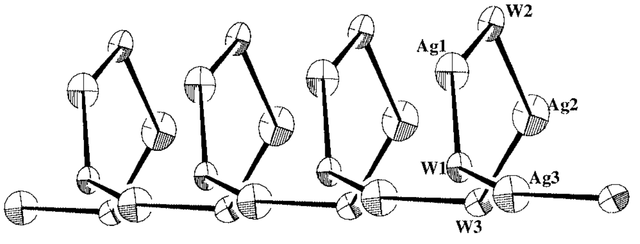

Fig. 9 The metal atoms in the helical chain anion $[W_3Ag_3S_{12}]^{3-}$. Reproduced from ref. 22.

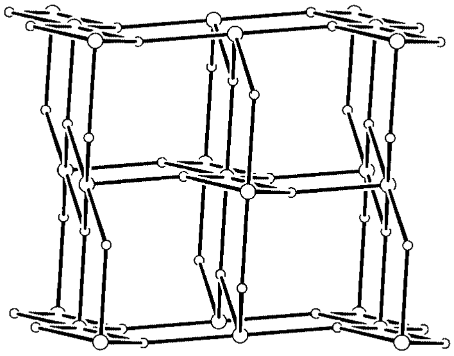

Fig. 10 The rutile-like framework in $M(tcm)_2$. Reproduced from ref. 28.

Prussian Blue is one of the oldest of all solid state co-ordination complexes[25,26] but other cyano-ligands only emerged from the Du Pont laboratories in the 1950s and 1960s. Particularly interesting examples in the context of magnetism are $C(CN)_2^-$ (dca) and $C(CN)_3^-$ (tcm).[27,28] The latter forms binary compounds $M(tcm)_2$ with most divalent 3d metal ions (M), as does dca, with connectivites analogous to that of rutile (Fig. 10), though to maximise space filling the structures consist of two such lattices interleaving one another. The $M(dca)_2$ series has a range of contrasting ground states: Cu is a paramagnet, and Ni and Co are ferromagnets. Substituting other ligands (which may be solvent molecules such as EtOH, H_2O, pyridine or DMF) to give $M(dca)_2L_2$ results in ribbons bridged by dca. As with most of the examples given in this article, we are certainly witnessing the emergence of a tip to a substantial iceberg here.

Conclusion

Given the range and variety of the topics discussed here, and of the examples used to illustrate them, it is hard (if not presumptuous) to draw overarching conclusions about solid state inorganic chemistry at the turn of the millennium, save for the trite but very positive one that it is in a state of extraordinary efflorescence. This is even more strongly reinforced by the list of topics not appearing here (and to whose protagonists I apologise) such as new complex oxides for superconductivity and magnetoresistance applications, insertion compounds for batteries, giant metal clusters such as nanoparticles and quantum dots, and many more. Choice is a personal matter, but the pages of *Dalton Transactions* at the end of the twentieth and beginning of the twenty-first century furnish ample material to show that our field of action, the Periodic Table, has many riches left to deliver. Watch this space!

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