

of opening up the structures of nature's aromatic stores, such as lignin and suberin.

The challenge for green chemistry is not just to replace undesirable chemicals such as chromates and polyhaloaromatics but also to make sure that, wherever possible, the substitutes and the chemistry used to manufacture them are green and sustainable. More research is currently needed to address the challenges that REACH and other product-focused legislation present — safer, more environmentally benign products are required in just about every commercial sector, with particular emphasis on flame retardants, plasticizers, adhesives and primers.

This new century will see a gradual transfer from a petroleum-based chemistry to a chemistry based on a wide diversity of feedstocks. Although virgin fossil-derived and mineral-derived resources will continue to be important for the foreseeable future, chemicals and materials derived from non-food biomass and from the increasing mountain of what we still refer to as 'waste' must take over: today's waste will be tomorrow's resource. Green chemistry can help in converting these feedstocks into resources through low-environmental-impact technologies, processes and methodologies. In this way we will be able to achieve the

essential goal for future generations of green and sustainable products. □

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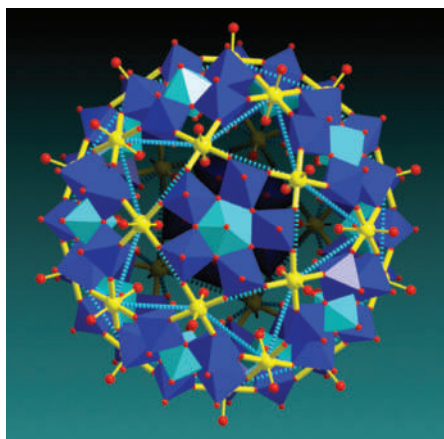
Predicting a structured future

If syntheses and structures can be more easily predicted, what will it mean for inorganic chemistry?

Achim Müller of the University of Bielefeld looks into his (quasi)crystal ball.

In a recently published essay¹, Jon McCleverty stated that “the developments in inorganic chemistry ... over the last 100 years have been awe-inspiring”. His article referred to examples such as the coordination chemistry of *s*-block elements based on macrocyclic polydentate ligands (initiating the development of supramolecular chemistry), bioinorganic chemistry (regarding the use of a variety of inorganic compounds in chemotherapy) and solid-state chemistry (leading to the discovery of high-temperature superconductivity). Most of these spectacular breakthroughs came from unexpected discoveries.

In the future, inorganic chemistry will continue to embrace materials, bioinorganic and environmental chemistry, as well as traditional areas such as catalysis. Furthermore, it will extend down to new length scales, controlling matter on the nanoscale. In my view the following three topics will be of central importance: (1) predictable syntheses in solid-state chemistry and — as the major point considered here — of nanosized multifunctional compounds/clusters, seeking to understand fully the relationship between structure and function (multifunctionality can only be realized by larger, nanosized, species²); (2) reactions under confined conditions, such as in nanopores/capsules, which is an area that might lead to fundamental discoveries, and (3) the realization of new aperiodic structures, as well as new bonding types and different reactivity paradigms. An underlying theme is in the prediction of inorganic structures. This is intrinsically difficult because of the extremely wide variety in



A missing link between the world of molecules and solids. This keplerate, $M'_{30}\{(Mo)Mo_5\}_{12}$ ($M' = Fe, Cr$) (ref. 4), is a spherical inorganic superfullerene. Its 12 $[(Mo)Mo_5O_{21}(H_2O)_6]^{6-}$ pentagonal ligands (blue polyhedra, O atoms red) are linked by 30 M' centres (yellow spheres), resulting in 20 corner-sharing M'_3 triangles like those in kagome lattices. The highlighted blue triangles form an Archimedean solid, an icosidodecahedron. Spherical periodicity is obtained because the linking of the 12 pentagons with five-fold symmetry — their centres span an icosahedron — cannot lead to translational periodicity, so the system itself resembles a quasicrystal.

structural motifs and geometries, which itself arises from the huge number of different chemical elements showing a range of bond properties and coordination numbers.

To illustrate the case of the predictable synthesis of multifunctional nanoparticles I shall consider soluble and stable spherical

metal-oxide-based nanocapsules². They have gateable pores, well-defined external surfaces and tunable internal ones; the latter can be of either an organic/hydrophobic or an inorganic/hydrophilic type and can influence the structure of encapsulated species². The capsules contain 12 metal-oxide-based pentagonal building blocks (pictured; comparable to the basic elements for spherical structures such as the C_{60} buckyball, icosahedral viruses or geodesic domes³). They can be linked by means of well-understood self-assembly processes: by either mononuclear spacers M' (such as Cr^{3+} and Fe^{3+}), leading to smaller capsules/pores⁴, or by dinuclear spacers ($Mo_2O_4^{2+}$), leading to larger ones³ (both with 120 equal metal–ligand bonds; pictured, yellow sticks). This is an example of real multifunctionality and recognizable structure–function relationships: the corner linking of the M'_3 triangles leads to magnetic frustration such as that found in kagome lattices (see ref. 4), whereas the presence of 20 gated pores with crown-ether function enables, for the larger capsules, the controlled take-up or release of alkali cations, mimicking biological transmembrane processes².

Molecules confined in nanopores react differently from those in homogeneous distributions. To study how a variety of encapsulated molecules react under the influence of different functional groups, appropriate inorganic capsules or 'nano-test-tubes' should be considered. Interestingly,

little is yet known about this, in contrast to organic chemistry, in which chemical transformations in (flexible) cages have been investigated⁵. Confined conditions can accelerate reactions — analogously to enzymes — or lead to new types of reactions altogether. A general challenge is to master energy and information on the nanoscale to create new technologies rivalling the complexity of living matter. This could be achieved, for example, through the discovery of different highly functionalized responsive species that can react specifically with their environment and self-assemble².

We now turn from discrete porous species to consider porous solids, such as metal–organic frameworks (MOFs): these materials are a promising new research area witnessing explosive growth and studied almost exclusively by inorganic chemists⁶. They have well-defined tunable cavities and surfaces, can be responsive to guests and can be orchestrated to trap, detect and even catalytically transform quite different species. Although until now MOFs have been studied mainly for storage (because of their large surface areas) and sieving, another role for them in the future could be their use as nanoreactors, allowing the production of a variety of interesting monodisperse nanoparticles⁶.

Solid-state syntheses have, until now, been assumed to be unpredictable, but even so they have led and will lead in the future to the discovery of materials with important properties and exotic phenomena. Future research in this field may initiate substantial technological advances, as well as breakthroughs in basic science. A new methodology for planning syntheses is on the way⁷, seeking to predict new targets

by computationally exploring the energy landscape above the configuration space of a given chemical system. This involves searching for global as well as local minima and ‘transferring’ the identified candidates to the thermodynamic space characterized by the respective hypersurfaces of free enthalpies; the procedure enables the successful candidate’s synthesis⁷. This could also include searching for links between structures of nanospecies and solids. For instance, the icosahedral quasicrystals mentioned in the next paragraph contain shells of atoms forming beautiful Platonic and (partly distorted) Archimedean solids⁸ such as the keplerates² (above; pictured).

One of the most exciting developments in solid-state inorganic chemistry has been the advent of aperiodic ordering, which caused a paradigmatic change. Experienced crystallographers — Linus Pauling included — argued vehemently against the proposed existence of quasicrystals. A weird and wonderful world of new phases and phenomena has since been reported. The best-studied class so far is that of the so-called Tsai-type phases⁸. These binary, stable, icosahedral quasicrystals are very interesting objects for future studies of structure–property relationships. In the wake of quasicrystals, a silent revolution has taken place regarding another class of aperiodic objects, namely incommensurately modulated phases. Some of these derive directly from the Tsai-type phases such as the modulated $\text{Ce}_{13}\text{Cd}_{58}$ (ref. 9). The extreme richness and complexity of the structural chemistry involved in these examples is astounding and unprecedented in the whole area of chemistry. We may be sure that new phenomena with possible applications

— especially related to complex surfaces — will be discovered in the field of aperiodic structures in the future.

I have discussed some classes of compounds in which interesting developments might be expected, such as solids with aperiodic ordering and confined chemistry in MOFs as well as multifunctional inorganic nanocapsules, with the potential for discovering new phenomena; I have also referred to the search for a rational design of syntheses and structures. However, chemists should always have their eyes open for interesting but unexpected phenomena that could open new avenues of research. It is also crucial to continue studying important technologies, such as the realization of artificial photosynthesis systems (particularly those for solar-driven water splitting to hydrogen), and working towards the discovery of compounds relevant for new pathways in catalysis using noble metals and oxygen (see ref. 10). □

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Thither supramolecular chemistry?

The way forward for a field in its infancy is to focus on complexity and integrated systems that may lead to emergent phenomena, suggests **J. Fraser Stoddart** at Northwestern University.

If the atoms are the letters, if the molecules are the words, and if the supermolecules are the phrases, then the language¹ we call chemistry took less than half a century to make the revolutionary transition from molecules to supermolecules, on the back of having taken well over a century to make the painstaking journey from atoms to molecules. If we peg the growth of chemistry to the expected lifespan of someone living in a developed country, then we are looking at no more than a two-year-old child who is just starting to string a few words

together. The chemist has still to learn how to construct sentences that adhere to some grammatical rules — that is, to introduce meaningful and helpful complexity at the simplest of levels into chemistry — and then acquire the skill set required to bridge, in a logical fashion, from sentence to sentence and so produce coherent paragraphs that ultimately tell a story when they are merged together in the form of a complete work.

Often, the seedlings of change are already planted in former times, yet they remain dormant within a community. So it

was with what became known² as supramolecular chemistry. Many would agree that it witnessed its formal beginnings with the appearance of Charles Pedersen’s seminal paper³ in *Journal of the American Chemical Society* in 1967. It fell, nonetheless, to the joint talents and ingenuity of Donald Cram⁴ and Jean-Marie Lehn⁵ to alert the chemical community at large to the generality and fundamental significance of a chemistry beyond