

Bringing inorganic chemistry to life

Achim Müller



In recent years, the development of advanced materials has been stimulated by the combinatorial strategies that Nature employs to construct assemblies of complex molecules with a specific form and function. Professor **Achim Müller** of the University of Bielefeld, Germany has extended this approach into the realm of inorganic chemistry in an extraordinarily imaginative way. He has been exploring the intricate and versatile chemical behaviour of molybdenum and its oxides, creating self-assembling systems of molybdates in solution that can be regarded as inorganic 'nanomodels' for biological activity at the cellular level.

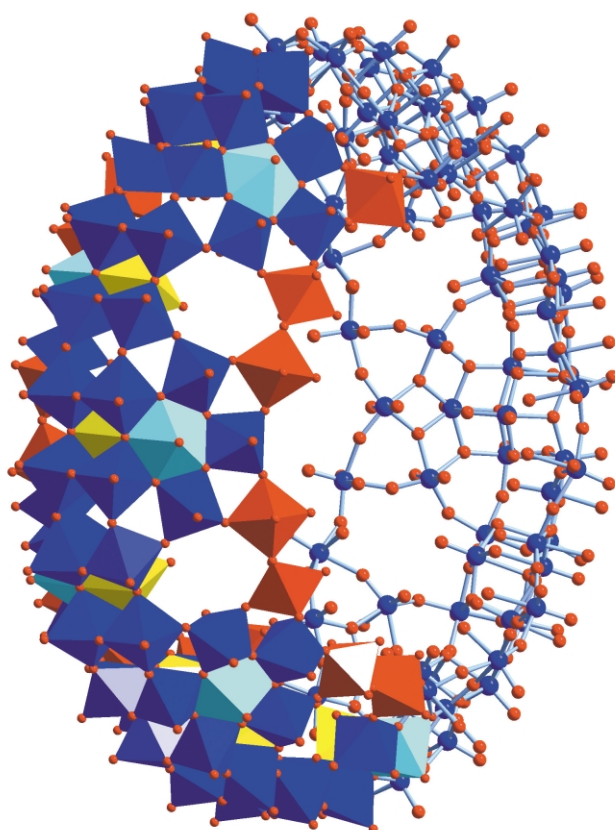


Fig. 1

The structure of the first published 'big wheel' containing 154 Mo atoms – half in polyhedral representation with different building units (Mo_8 blue, Mo_2 red, Mo_1 yellow), and half in ball and stick representation (Mo blue, O red)

EVERYONE is probably familiar with the intense blue colour obtained when acidified solutions of molybdate (Mo^{VI}), or a suspension of molybdenum oxide (MoO_3) in water, are treated with a reducing agent such as stannous (Sn^{II}) ions, sulfur dioxide or hydrazine (N_2H_4). It is used as the basis for sensitive colorimetric tests for phosphate and arsenate ions and tin. For at least two centuries, since 'molybdenum blue' was first studied by Carl Scheele and Jöns Berzelius, chemists have puzzled over the nature of the molybdenum species that the solution contains. It is a substance or group of substances about which there has been much discussion.¹ As a leading researcher in synthesising and characterising soluble metal oxides and sulfides, Professor Müller was also fascinated by molybdenum blue solutions. By probing its remarkable structure, he has shown that it unlocks the door to a new inorganic world paralleling that of biology.

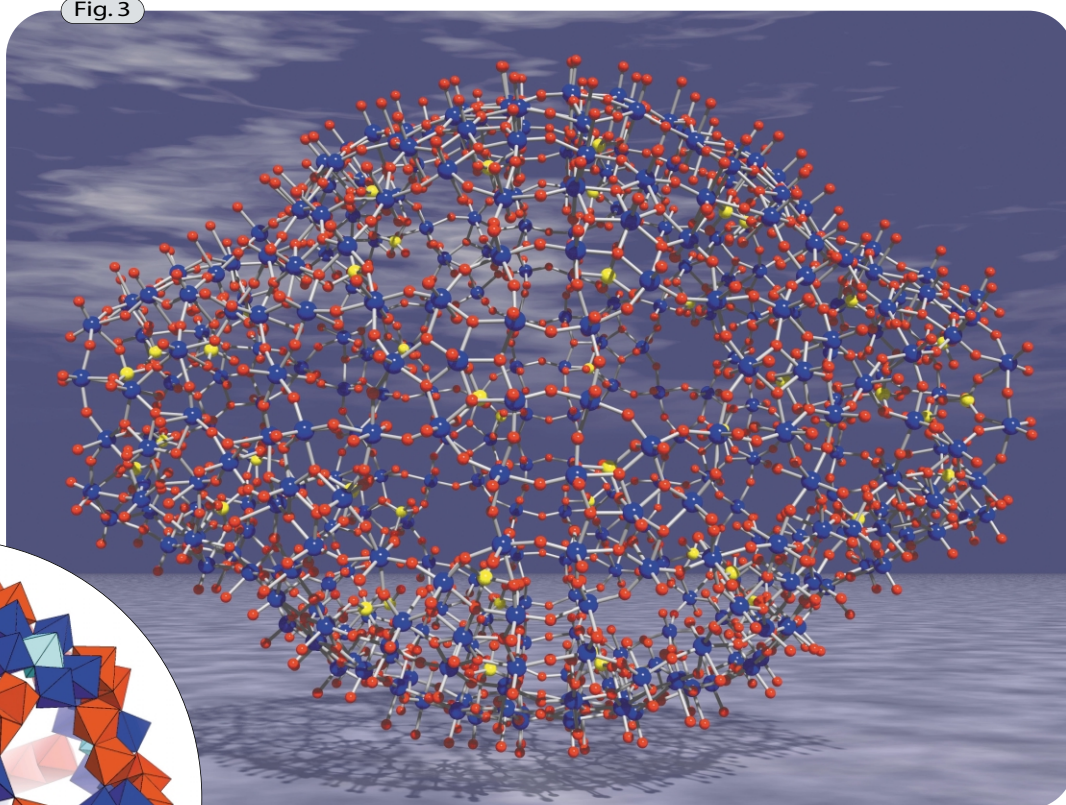
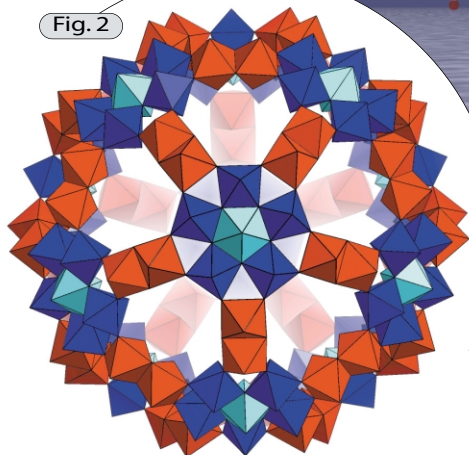
The complex world of molybdenum

The chemistry of molybdenum oxides and the soluble molybdates has long been recognised as extremely complex – as a quick look in any inorganic textbook will attest. The formation of distinct molybdenum-oxygen species is strongly dependent on environmental conditions. One of the most important basic building blocks are MoO_6 octahedra which can

Fig. 3

Fig. 3 The Mo₃₆₈-type nano-hedgehog (Mo blue, O red, S yellow)Fig. 2 The first published Keplerate, an inorganic superfullerene built up by 12 pentagonal Mo based units (blue) and 30 different Mo₂-based linkers (red)

Fig. 2



share the oxygen corners or edges.² Studies showed that molybdenum blue appeared to contain clusters of these building blocks as well as cluster assemblies large enough to scatter light from a laser.³

In the early 1990s, Müller's group worked on characterising molybdenum blue and optimising its preparation. They were able to obtain a single crystal of the material and, using a range of analytical techniques, reveal that it was constituted from the most breathtaking molecular assemblies – giant cyclic polyoxomolybdates, 4 nanometres wide (Fig. 1). Each molecule was made up of a total of 154 molybdenum atoms embedded in a network of oxygen atoms. Dubbed the 'Bielefeld giant wheel', it was at that time the largest inorganic molecular cluster ever characterised.^{4,5} Since then, wheel-shaped clusters with 176 and 248 molybdenum atoms have also been obtained.⁶

Not surprisingly, the paper on the Bielefeld giant wheel, published in 1995, attracted considerable attention. At the same time, Müller saw the possible directions in which the research could go. "I realised," says Müller, "that this

aqueous solution of molybdate was unique in the sense that it pointed the way to a dynamical library of complex structures." Linking the molybdenum-oxygen building blocks in different ways would lead to a "combinatorial explosion of materials". The subunits can be formally compared to amino acids which link to form proteins, adds Müller.⁷ Two units can be joined *via* a condensation process – analogous to that in peptide formation. Protonation is the condition for linking and the size of the cluster is controlled by the pH. Müller points out that such structures can be made to self-assemble in aqueous solution in a controllable and tunable way "under varying but well-defined reducing conditions".

Müller and his team went on to create the most marvellous highly symmetric ball-shaped structures, incorporating pentagonal bipyramidal components (MoO₇) as the directing units (Fig. 2).⁸ While the octahedral units look like two Egyptian pyramids with their bases stuck together, the pentagonal bipyramidal structures have five edges around the centre instead of four. These can share edges with five MoO₆ octahedra to create pentagonal molybdenum-based units. This is obviously significant in building up football-shaped structures, and useful analogies can be drawn with the carbon fullerenes which are also based on pentagonal units. The first of these

molybdenum superfullerenes, or 'Keplerates' as Müller calls them, was made in 1998. (The ball-shaped species contain fragments formally comparable to the early cosmos of Johannes Kepler.) It was composed of a hollow sphere of 132 molybdenum atoms with an inner cluster of 60 molybdenum atoms arranged like the C₆₀ bucky-ball. Müller points out that the arrangements of the subunits in such structures are reminiscent of the packing of protein molecules on the surface of a spherical virus.

More recently, the Bielefeld team prepared a huge cluster which they call a 'nano-hedgehog' because of its shape and as it has an outer layer of oxygen atoms pointing outwards (Fig. 3). It contains 368 molybdenum atoms and is actually the size of a protein.⁷ It has an internal cavity 2.5 nanometres wide and 4 nanometres long which encapsulates about 400 water molecules. The electron-rich structure is deep blue in colour – due to delocalised electrons. Müller believes that such structures could be used as selective catalysts, similar to zeolites, or as nanoreactors.

Müller's aim has thus been to explore how the functionality of such materials could be explored through tuning the structure by varying the reaction conditions and reagents. One combination of conditions created spherical clusters with an exotic host-guest topology

suggesting potential use in molecular electronics. The starting material was a solution of the well-known Keggin anions of the type $[\text{PMo}_{12}\text{O}_{40}]^{3-}$, formed from phosphate and molybdate. These are normally stable, but in the presence of iron(III) ions (and acetate), they decompose to form giant icosahedral clusters composed of pentagonal molybdate building blocks linked by hydrated iron(III) groups. Remaining Keggin anions are just the right size to be encapsulated inside the cluster shell (Fig. 4).⁹ Müller notes that the higher symmetry of the icosahedral cluster wins out over the lower symmetry of the independent Keggin ions in a Darwinian competition to form a supramolecular structure somewhat analogous to the first spherical protocells that may have formed on Earth.

The final result is a bizarre electronic structure consisting of a polyhedral molybdenum-iron magnetic dot – rendered paramagnetic by the presence of 30 iron ions, hosting a noncovalently-bonded Keggin ion guest which behaves like a quantum dot in that it possesses discrete electronic energy levels. In the solid state, the nanosized-clusters crosslink *via* iron-oxygen bonds to form a two-dimensional network of magnetic dots which represent the strongest paramagnetic molecular material known today – each cluster has 150 unpaired electrons. Derivatives of such systems could act as elements of magnetic or electronic storage devices. Müller envisages that this type of ‘crystal engineering’ will lead to novel composites containing arrays of clusters whose electronic or other properties can be tuned depending on the constituents used. This is especially valid as not only extended structures but also molecular assemblies, *i.e.* oligomers of the single neutral cluster can be obtained.¹⁰

Inorganic receptors

A current challenge in nanotechnology is to mimic molecular recognition that characterises biological regulation. The highly soluble Keplerates offer an ideal inorganic model for investigating the associated structural and dynamical changes. Recently, Müller and his team have synthesised giant molybdenum oxide-based nanoclusters with tailor-made pores.^{11,12} These ‘nanosponges’ are created from the basic pentagonal units connected with different linkers in the form $[(\text{pent})_{12}(\text{link})_{30}]$, the pore as well as the overall size depending on the length and charge of the linker. Spherical systems containing 20 pores corresponding to Mo_9O_9 rings with a diameter between 0.6 and 0.8 nanometres have been prepared.¹¹ The system, with its 12 pentagonal units and Mo-Mo linkers generated from two edge-shared MoO_6 octahedra (*i.e.* linkers are made from a total of 60 octahedra), is structurally the inorganic analogue of the simplest icosahedral virus.

Such systems show behaviour analogous to simple cell responses. The pores can be closed by cations of the appropriate size and shape, in this case guanidinium cations (Fig. 5a). Guanidine is of interest as it is used in a variety of industrial and pharmaceutical processes. Its functional group occurs in an amino acid and can be also regarded as a useful anion receptor. Other clusters containing mononuclear linkers, for example, iron(III) or vanadium(IV) generate smaller pores created from Mo_6O_6 rings. These are the right size to capture potassium ions (Fig. 5b), in a manner corresponding to the supramolecular behaviour shown by crownethers – although repeated 20 times over!¹²

What is particularly remarkable is that closing the pores induces changes in the structure of the droplet of water trapped inside the cluster. The water molecules become arranged in highly symmetrical endohedral clusters (Fig. 6). ‘This effect can be compared with signal transduction by

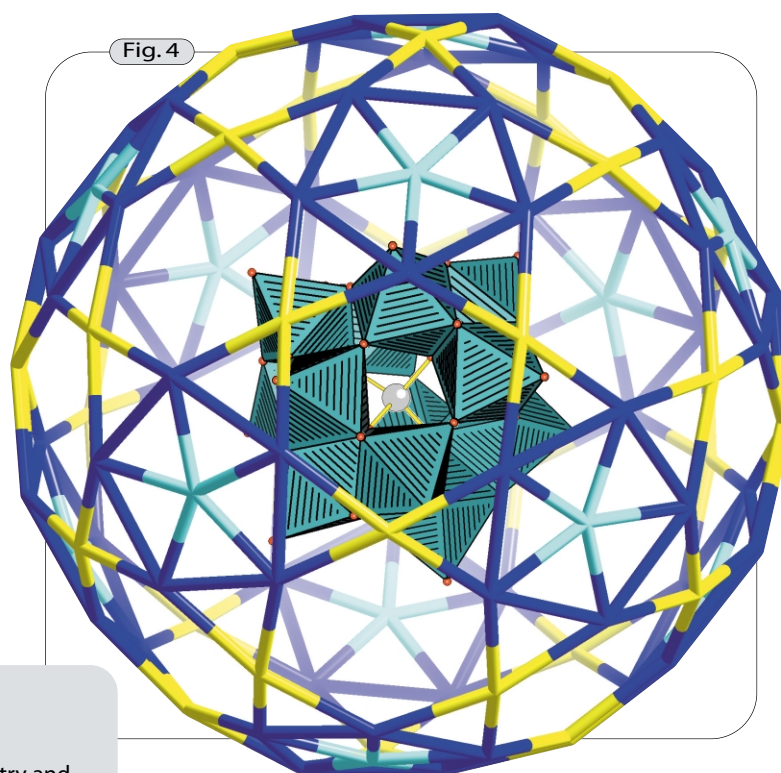


Fig. 4

Fig. 4 A Keggin-cluster encapsulated in a Keplerate (wire-frame representation): the 30 Fe^{III} centres act as linkers (yellow) for the 12 Mo-based pentagonal units (blue)

Biography

Professor Müller first studied chemistry and physics at the University of Göttingen, becoming Associate Professor at the University of Dortmund in 1971, and later in 1977, Professor of Inorganic Chemistry at the University of Bielefeld. He maintains an extremely broad range of interests, ranging from studies into soluble metal oxides and sulfides through spectroscopic techniques to biological nitrogen fixation.

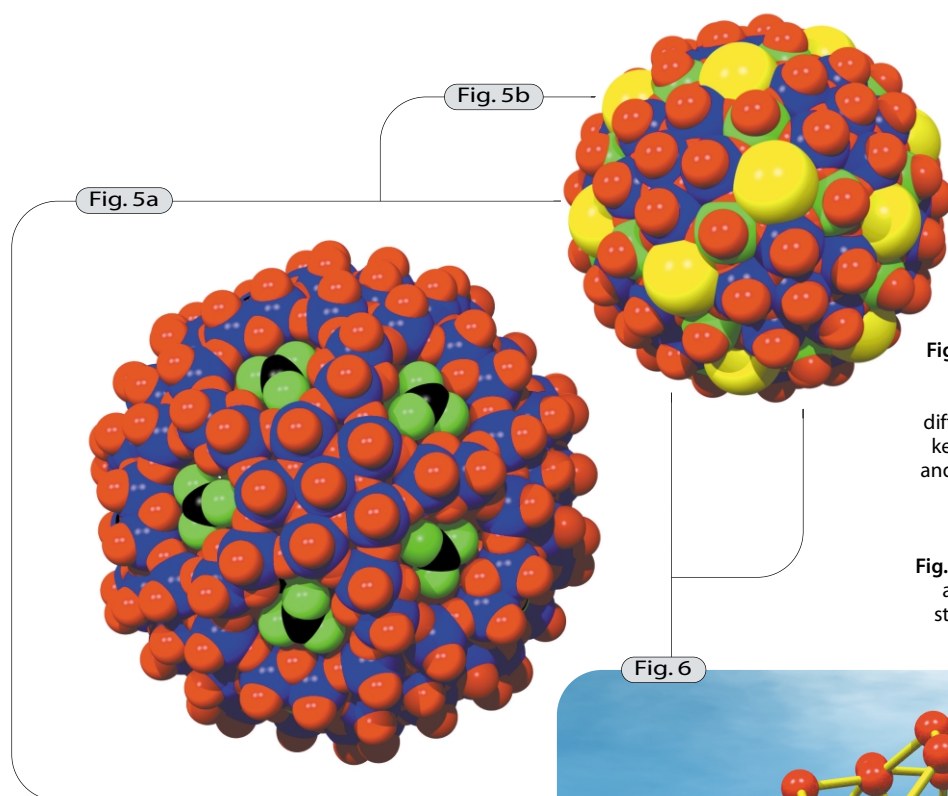


Fig. 5 Structures of two 'nanosponges' of the type $(\text{pent})_{12}(\text{link})_{30}$ (space-filling representation). The 20 pores have different sizes and illustrate the 'lock and key' principle between the sponge/host and its 20 guests: K^+ (a) and guanidinium cations (b) (Mo blue, O red, N green, C black, K yellow, linker in (b) green)

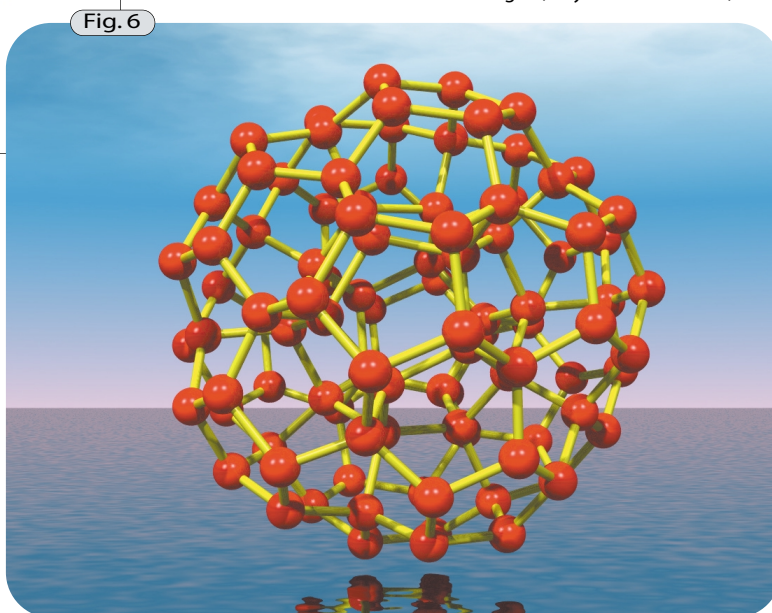


Fig. 6 A possible snapshot of liquid water: a nanodrop of water with well-defined structure encapsulated in the Keplerate of Fig. 2 (only O atoms shown)

which a cell converts an extracellular signal into a response," says Müller. Furthermore, studies of encapsulated assemblies of water molecules could offer a useful tool in exploring water's complex phases. The structure of water in biological systems, in particular, is still not well understood but known to be significant in mediating protein conformation, for example.

The molybdate clusters, derived from studies of molybdenum blue, have turned out to exhibit an extraordinarily rich behaviour which has a bearing on many aspects of chemical research today: coordination chemistry, catalysis, advanced material design, molecular electronics, crystal engineering, single-molecule chemistry (perhaps?), nanochemistry in the real sense, surface modelling and supramolecular chemistry.¹³ However, what is unique about these complex inorganic systems is that not only do they form an almost limitless variety of structures in which form and function can be closely correlated, but most important, they are stable, flexible macromolecules which are highly soluble in water, and which maintain their structure and functionality while in a mobile state so that chemical reactions can be performed at specific sites. This means that they are singularly equipped to mimic biological processes. As Professor Müller says: "With these materials we are bringing inorganic chemistry to life."

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