ChemComm
FEATURE ARTICLE

A variety of combinatorially linkable units as disposition:† from a giant icosahedral Keplerate to multi-functional metal–oxide based network structures

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Received (in Cambridge, UK) 22nd February 1999, Accepted 20th April 1999

In polyoxometalate chemistry a large variety of compounds, clusters and solid-state structures can be formed by linking together metal–oxygen building blocks. Interestingly, reactions based on libraries of virtual building blocks can be planned under appropriate conditions, resulting for instance in the high-yield synthesis of inorganic superfullerenes and giant ring-shaped, electron-rich, mixed-valence polyoxomolybdates with nanosized cavities. The latter species can continue to grow and also can be covalently linked together to form chains as well as layered mesoporous compounds with properties relevant for materials science. The largest polyoxometalate cluster obtained on the basis of such a growth process consists of 248 Mo atoms. Remarkably, such giant ring species can also act as hosts for other clusters forming new types of supramolecular compounds.

Introduction

In nature, complex molecular systems like proteins have evolved (*natura naturans*) which are perfectly suited to their functions. These are formed, at least formally, in a sequence of steps principally under dissipative conditions, that is far from thermodynamic equilibrium. The challenge for the chemist is to synthesize correspondingly complex multi-functional molecules also under non-dissipative conditions using one-pot reactions, without the need to separate and purify each single intermediate product. Relevant model reactions have been explored in solutions of simple oxoanions of the early transition metals. Novel types of molecular growth processes including a type of induced cascade and those with feedback effects have been discovered leading to a huge variety of unusual compounds regarding structures and properties.[1] The basis is constituted by a system with a variety of combinatorially linkable polyoxometalate building units either as existing or virtual species (as disposition) which are available on demand in a kind of 'library' depending on the boundary conditions.

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In search of an archetypical system with linkable units as disposition: the generation of a superfullerene (giant ball) with more than 500 atoms and icosahedral symmetry as a relevant example

While molecular systems, even relatively large ones, can in principle be generated by successive steps of synthesis and isolation,[2] the formation of extremely large molecular systems, in particular those with unusual structures, properties, together with very high symmetry, *e.g.* those comparable to simple spherical viruses, requires a different method of approach.

If we intend to construct for instance a giant species similar in size and shape to spherical viruses with icosahedral (C_5 C_3 C_2) symmetry, we have to find a reaction system in which pentagonal units can first be generated, then get linked and be placed at the 12 corners of an icosahedron. In the case of polyoxomolybdates these pentagonal units ($\{(Mo)Mo_5\}$ groups) consist of a central bipyramidal MoO_7 unit sharing edges with five MoO_6 octahedra. The $\{(Mo)Mo_5\}$ unit is a constituent of the $\{Mo_8\}$-type unit abundant in many giant polyoxometalates (see below) in which, apart from the related densely packed $\{(Mo)Mo_5\}$ unit, two more loosely bound MoO_6 octahedra occur. When linkers in the form of *doubly bridging units* are present in solution, for instance those of the classical $\{Mo^{V}_2O_4\}^{2+}$ type[3] (typically formed in reduced molybdate solutions in the presence of bidentate ligands) that can link these pentagonal units, an icosahedral molecular system with 12 of the mentioned pentagons and 30 of the mentioned linkers is formed. When for example acetate anions act as bridging ligands for the $\{Mo^{V}_2O_4\}^{2+}$ groups, the spherical cluster with the stoichiometry $[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(MeCO_2)_{30}(H_2O)_{72}]^{42-}$ ($\{Mo_{132}\}$) results,[4] where the central Mo positions of the $\{(Mo)Mo_5\}$ pentagons define the 12 corners, and the $\{Mo^{V}_2O_4\}^{2+}$ groups the 30 edges of an icosahedron (in agreement with Euler's well known formula). This corresponds to the formulation $[\{(Mo)Mo_5O_{21}(H_2O)_6\}_{12}\{Mo^{V}_2O_4(MeCO_2)\}_{30}]^{42-}$. Interestingly, the ball-like structure (Fig. 1) is also documented in the crystal structure (space group $Fm\bar{3}$) with cubic closest packed spheres of the salt $(NH_4)_{42}[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(MeCO_2)_{30}$-

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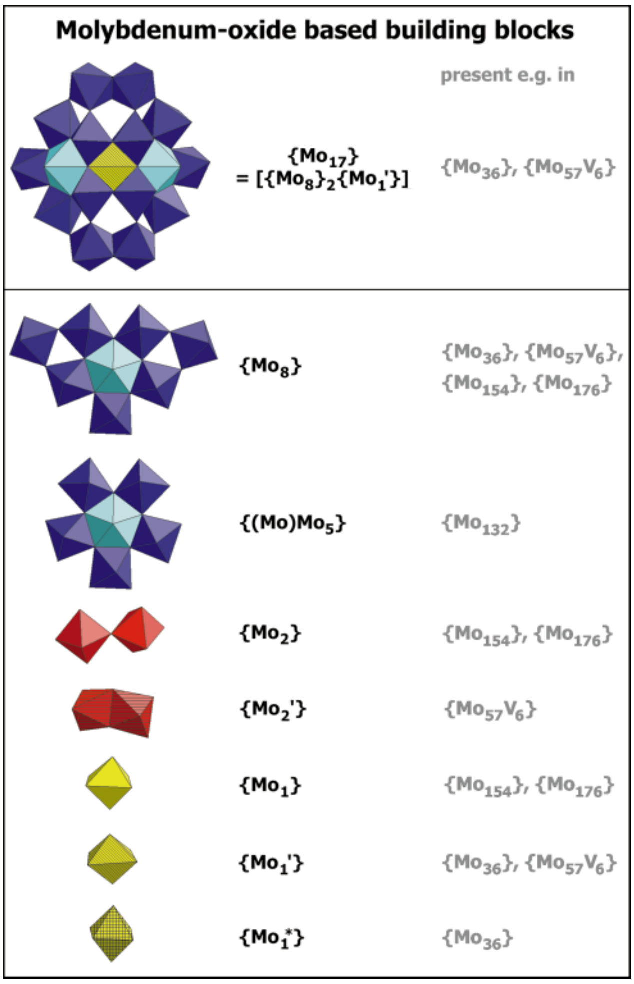
† A disposition can be interpreted as the inherent tendency of an object or system (in this case molecules or ions or fragments of these) to act or react under certain characteristic conditions.



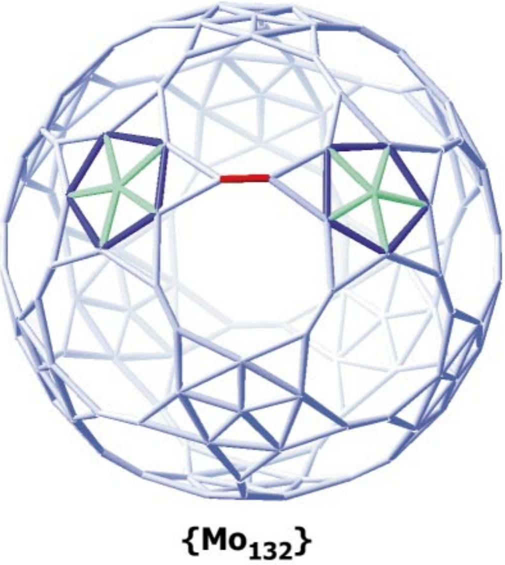


Fig. 1 Schematic representation of the 132 molybdenum atom framework of the Keplerate cluster highlighting its spherical nature. Two pentagonal $\{(Mo)Mo_5\}$ groups (blue) linked by an $\{Mo^V\text{–}Mo^V\}$ bridge (red) are emphasized.

$(H_2O)_{72}]\cdot xH_2O\cdot yMeCO_2NH_4$ ($x \approx 300$, $y \approx 10$). Remarkably, we are speaking about a molecular system having icosahedral symmetry although it is built up from more than 500 atoms. Despite the large number of normal vibrations the Raman spectrum shows just a few lines because only the A_g and the fivefold degenerate H_g modes are Raman active (Fig. 2).

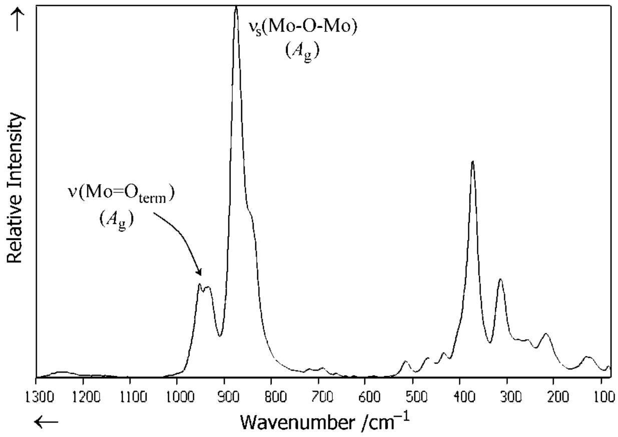


Fig. 2 Raman spectrum of $(NH_4)_{42}[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(MeCO_2)_{30}(H_2O)_{72}]\cdot xH_2O\cdot yMeCO_2NH_4$ ($x \approx 300$, $y \approx 10$) (powder, λ_e = 1064 nm; ν_s stands for breathing).

This molecular system with 60 MoO_6 subunits or 12 related $\{(Mo)Mo_5\}$ pentagons represents a topological model for spherical viruses, *e.g.* the most simple satellite tobacco necrosis virus (STNV) with 60 identical protein subunits (coded only by one gene) or 12 pentagonal capsomers (morphology units), each capsomer consisting of five protomers (for details see ref. 5 and Fig. 3). The wire-frame representation of the $\{Mo_{132}\}$ cluster species additionally even suggests the structural/topological similarity to the more complex icosahedral virus capsids with a triangulation number of $T = 3$ (Fig. 4) (for details of virus structures and topologies see ref. 5 and 6).

More interestingly, on substituting the bridging acetate ligands by formate groups this smaller ligand allows a special type of organization of the *ca.* 60 encapsulated H_2O molecules: a related hydrogen-bonded cluster as guest system with an 'onion-type' structure which is induced by the peripheral spherical cluster shell (Fig. 5).[7]

It has been proposed to call the $\{Mo_{132}\}$-type cluster a Keplerate corresponding to Kepler's model of the cosmos and his concept of planetary motion, as described in his early opus *Mysterium Cosmographicum*.[8] In accordance with this speculative model, Kepler believed that the distances between the orbits of the planets could be explained if the ratios between the successive orbits were designed to be equivalent to the spheres successively circumscribed around and inscribed within the five Platonic solids. In analogy, the cluster correspondingly shows a spherical shell of terminal oxygen atoms in which an icosahedron spanned by the centers of the 12 $\{(Mo)Mo_5\}$ pentagons, the Mo atoms of the central MoO_7 bipyramids, is inscribed (see Fig. 1).

We are convinced that this $\{Mo_{132}\}$-type cluster will be the starting point for the development of a Keplerate-type chemistry, also due to the fact that these types of species are stable in aqueous solution and allow the encapsulation of different types of guests into the cavity. Furthermore, a collection of the spherically shaped huge clusters is a useful model system for special dynamical aspects of solid-state chemistry, since it enables for instance the investigation of nucleation processes (which are still not understood) but probably also of the first principles of structure-forming processes.

With respect to this fascinating discovery of the giant icosahedral cluster it seems worthwhile to concentrate on general aspects of self-aggregation processes, especially those based on the relevant polyoxometalate library systems (for aspects of combinatorial chemistry see ref. 9). In these systems we can expect reaction pathways which will lead to an extreme variety of unusual molecular systems based on differently linkable virtual units as disposition in solution.

The route to nanoscaled structures

If such unusual species as the mentioned Keplerate can be formed by linking different well defined units as disposition, it

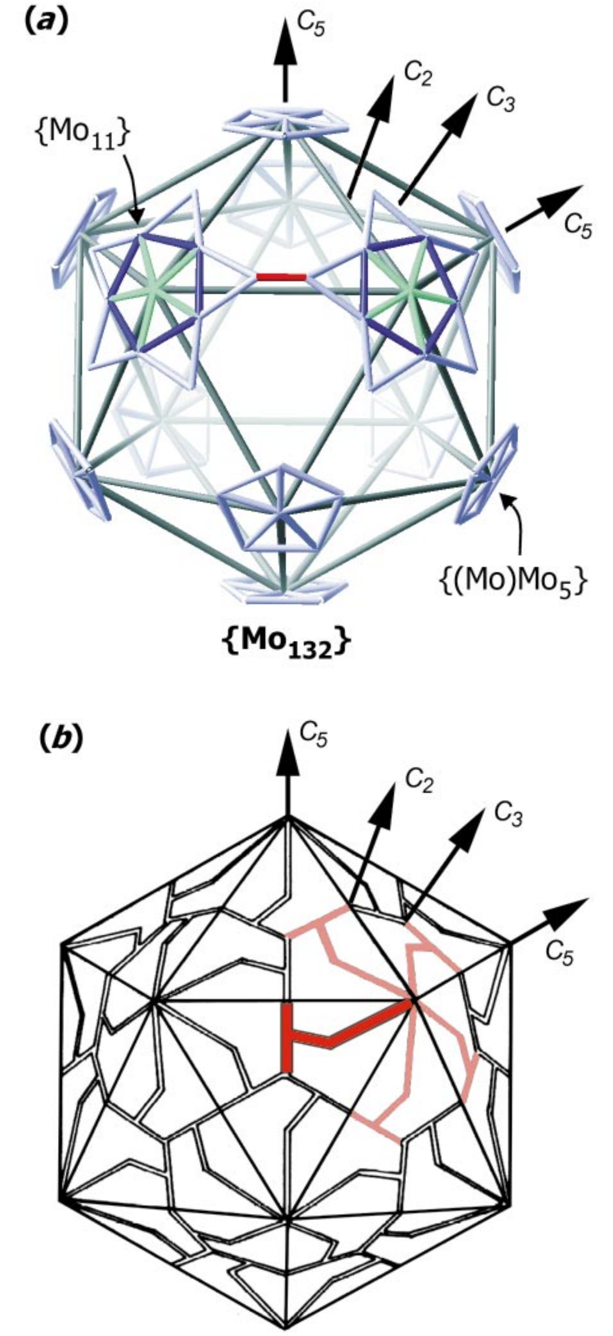


Fig. 3 Schematic representation of the icosahedron spanned by the centers of the $\{(Mo)Mo_5\}$ subfragments of the $\{Mo_{132}\}$-type cluster (*a*) and of the satellite tobacco necrosis virus with triangulation number $T = 1$ (ref. 5) highlighting five of the protomers (red) (*b*). Two $\{Mo_{11}\}$ units each formed by the $\{(Mo)Mo_5\}$ groups and the five related Mo centers of the five neighbouring $\{Mo^V_2O_4\}^{2+}$ bridges are emphasized.

is worthwhile to have a look at conditions which favour the corresponding emergence of molecular complexity including synthetic routes involving several successive reaction steps.

Optimal conditions for linking of fragments are:

- abundance of a huge variety of linkable units, *i.e.* building blocks and
- the possibility of generation of units (intermediates) with high free enthalpy to drive polymerization or growth processes, *e.g.* by formation of H_2O, of an easy structural change in the building units and blocks, of including hetero elements in the fragments, to form larger units which can be linked in different ways, to control the structure-forming processes by templates, to generate structural defects in reaction intermediates (*e.g.* leading to lacunary structures) in order to remove building units from large intermediates by the presence of appropriate reactants, to localize and delocalize electrons in different ways in order to gain versatility, to control and vary the charge of building parts (*e.g.* by protonation, electron transfer reactions, or substitution) and to limit growth by the abundance of appropriate terminal ligands, of generating fragments with energetically low-lying unoccupied molecular orbitals.

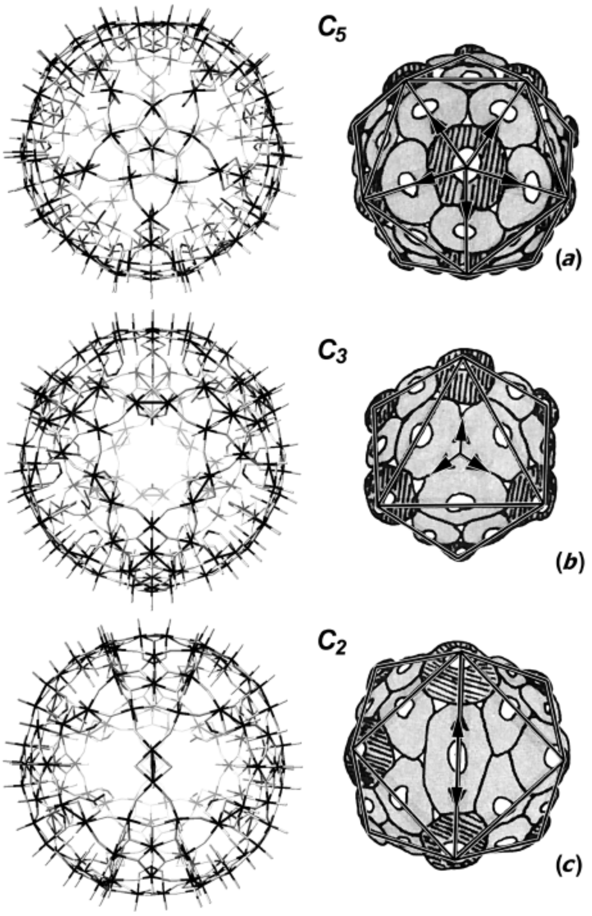


Fig. 4 Illustration of the structure of the $\{Mo_{132}\}$-type cluster (left) with perspective views along a fivefold (*a*), a threefold (*b*), and a twofold (*c*) symmetry axis in wire-frame presentations (used due to the structural complexity). For the purpose of comparison, corresponding schematic representations of an icosahedral virus capsid ($T = 3$) with 20 hexagonal and 12 pentagonal capsomers (morphology units) are presented [see ref. 6(*c*)]. In both systems, the C_5 axes cross the centers of the pentagonal units (hatched) (*a*), the C_3 axes cross the midpoint between three units (*b*), and the C_2 axes cross the center of the units (*c*). Whereas (*a*) refers to the centers of both the pentagonal $\{(Mo)Mo_5\}$ units and the pentagonal capsomers which are located at the 12 corners of an icosahedron (see Fig. 3), (*b*) and (*c*) refer to the $\{Mo^V_2\}$ units of the $\{Mo_{132}\}$-type cluster and the hexagonal capsomers, respectively.

According to our present knowledge these conditions can only be optimally fulfilled in polyoxometalate systems which possess the relevant variety of molecular and electronic configurations, and not *e.g.* in silicate-based systems.

In generating large complex molecular species we have to realize that corresponding natural processes are effected by the (directed as well as non-directed) linking of (a huge variety of) basic and well defined preorganized (or stepwise organized) fragments. An impressive example of this, discussed in almost all textbooks on biochemistry, is the self-aggregation (reconstitution) process of the tobacco mosaic virus (TMV), which is based on preorganized units.[10] *This process more or less meets our strategy in controlling the linking of fragments to form larger units and linking the latter again.* The linking of building blocks containing 17 metal atoms ($\{Mo_{17}\}$ units) to form cluster anions consisting of two or three of these units provides an archetypical example. The resulting two- or three-fragment

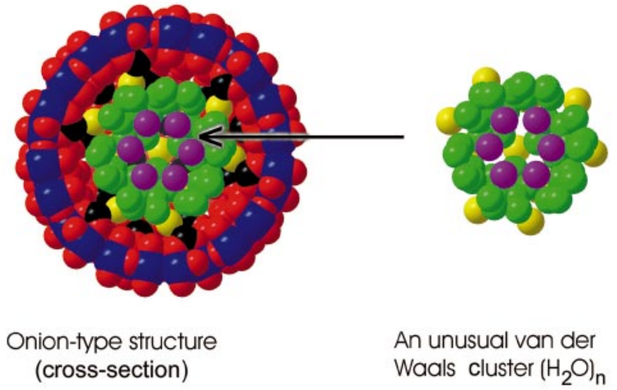


Fig. 5 Cross section through the equator of $[(H_2O)_n \subset Mo^{VI}_{72}Mo^{V}_{60}O_{372}(HCO_2)_{30}(H_2O)_{72}]^{42-}$ allowing a view into the cavity of the cluster shell and highlighting the hydrogen-bonded cluster formed by the encapsulated H_2O molecules (oxygen atoms) (*left*). The different shells spanned by encapsulated H_2O molecules are represented by spheres with different colours [violet shell (radius *ca*. 3.5 Å), green shell (6.2–6.9 Å) and yellow shell (8.2–8.7 Å) (*right*)]. Interestingly, the onion-like structure of the whole anion is completed by the three following outer shells consisting of (1) that of the 72 H_2O and 30 formate ligands coordinated to molybdenum atoms and pointing into the cavity (*ca* 10.5 Å), (2) that of the 132 molybdenum atoms (*ca* 13.1 Å) and (3) that of the terminal 132 oxygen atoms (*ca* 14.7 Å) (Mo centers: blue, O atoms: red, C atoms: black).

clusters are of the $\{Mo_{36}\}$ ($[\{MoO_2\}_2\{H_{12}Mo_{17}(NO)_2O_{58}(H_2O)_2\}_2]^{12-} = [\{Mo_1^*\}_2(\{Mo_8\}_2\{Mo_1'\})_2]$) or of the $\{Mo_{57}M_6\}$ type (*e.g.* $[\{VO(H_2O)\}_6\{Mo_2(\mu\text{-}H_2O)_2(\mu\text{-}OH)\}_3\{Mo_{17}(NO)_2O_{58}(H_2O)_2\}_3]^{21-} = [\{VO(H_2O)\}_6\{Mo_2'\}_3(\{Mo_8\}_2\{Mo_1'\})_3]$) (Fig. 6).[11,12]

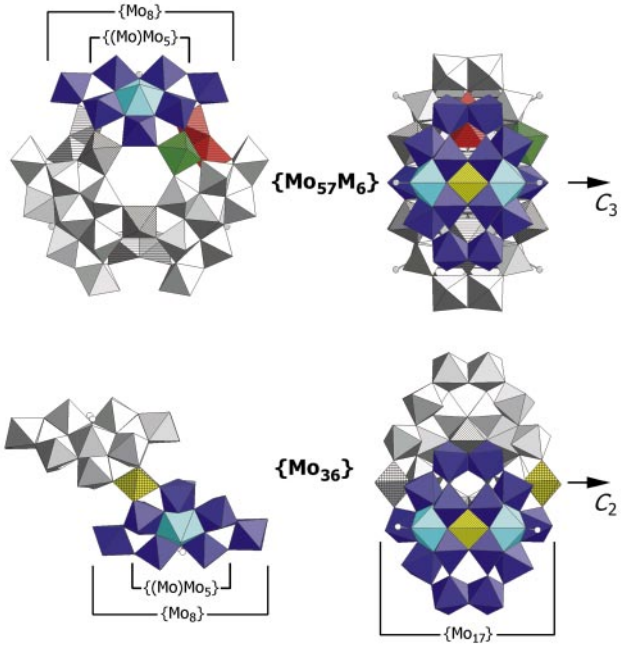


Fig. 6 Polyhedral representation of the $\{Mo_{57}M_6\}$ cluster with its basic building blocks and their constituents along the C_3 (*upper left*) and along one of the three C_2 axes (*upper right*): On the upper right, one $\{Mo_{17}\}$ building block consisting of one $\{Mo_1'\}$ and two $\{Mo_8\}$ groups, and on the upper left, one $\{Mo_8\}$ unit is shown in colour. Also shown in colour are one $\{Mo_2'\}$ group (built up from two face-sharing octahedra) and one MO_6 unit (green, cross-hatched). For comparison, the polyhedral representations of the $\{Mo_{36}\}$ cluster structure, consisting of two $\{Mo_{17}\}$ building blocks linked by two $\{Mo_1^*\}$ units (only one in colour), are shown in the related views, also highlighting one $\{Mo_8\}$ (*bottom left*) and one $\{Mo_{17}\}$ building block (*bottom right*). Of importance is the relation between $\{Mo_8\}$ and the pentagonal $\{(Mo)Mo_5\}$ groups (see text) ($\{Mo_8\}$: blue (central MoO_7 pentagonal bipyramid: cyan), $\{Mo_2'\}$: red hatched, $\{Mo_1'\}$: yellow hatched, $\{Mo_1^*\}$: yellow, cross-hatched).

The structure of the $\{Mo_{17}\}$ unit can furthermore be reduced to two $\{Mo_8\}$-type groups which are symmetrically linked by an $\{Mo_1'\}$-type unit. The $\{Mo_8\}$ building block, found in many other large polyoxometalate structures, is itself (as mentioned above) built up by a densely packed pentagonal $\{(Mo)Mo_5\}$ unit, containing a central MoO_7 or $MoO_6(NO)$ bipyramid sharing edges with five MoO_6 octahedra, and two more weakly bonded (sharing only corners) MoO_6 octahedra which can be more easily ‘removed’. The pentagonal unit with a high formation tendency is for instance responsible for the formation of structures with icosahedral symmetry like the $\{Mo_{132}\}$-type cluster (for details, see Fig. 1).

With the $\{Mo_8\}$-type building block even very large and unusual clusters can be built up: subsequent to our publication[13] of a 3.5 nm-diameter wheel-shaped metal–oxide based cluster anion containing 154 molybdenum atoms *i.e.* $[Mo_{154}(NO)_{14}O_{448}H_{14}(H_2O)_{70}]^{28-}$ ($\{Mo_{154}\}$) and built up from 14 of the mentioned $\{Mo_8\}$ groups linked by 14 $\{Mo_2\}$- and 14 $\{Mo_1\}$-type units, respectively (Fig. 7,8), it was metaphorically stated in *New Scientist*

> “Big wheel rolls back the molecular frontier”.[14]

This signifies the enormous interest of modern chemistry to ‘leave’ the molecular world, characterized by rather small molecules or ions, and to ‘proceed’ to the meso- or nano-world with a view to discovering and investigating the new inherent phenomena and system qualities.

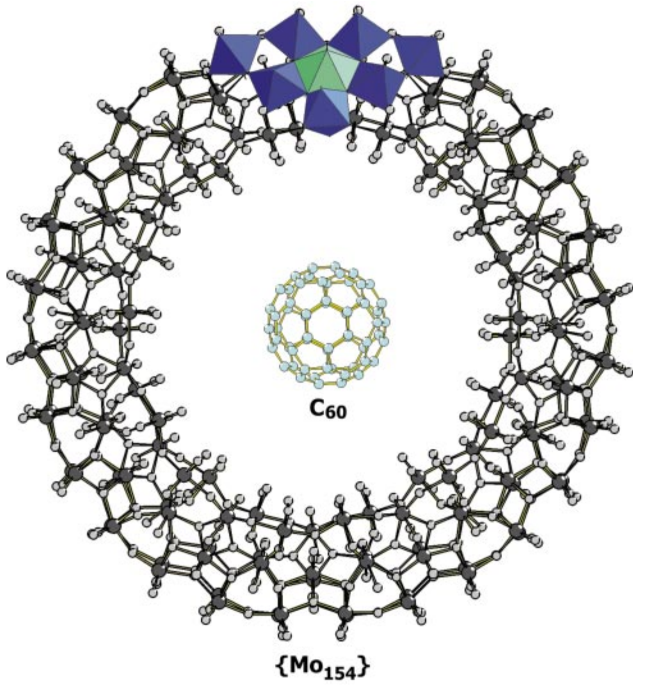


Fig. 7 Ball-and-stick representation of the $\{Mo_{154}\}$-type cluster $[Mo^{VI}_{126}Mo^{V}_{28}O_{462}H_{14}(H_2O)_{70}]^{14-}$ showing one $\{Mo_8\}$ unit (blue) with its central MoO_7 pentagonal bipyramid (cyan) in polyhedral representation. For the purpose of size-comparison, a C_{60} fullerene molecule is shown.

Remarkable is that *using the same reaction type*, i.e. *the acidification of aqueous solutions of the most simple tetrahedral oxoanions of the early transition elements of the type* MO_4^{n-}, *the resulting products span the three important areas of matter*, from the micro-, through the meso- (or nano-) to the macrostructures, the latter being characterized by crystallinity or translational invariance. In the present case the nanostructures are of particular interest owing to the huge structural variety of the related polyoxometalates. Additional external chemical interventions, *e.g.* those corresponding to the list given above, lead to an even greater structural diversity, for example in the presence of reducing agents (especially those with the possibility of multi-electron transfer), appropriate templates or hetero elements.

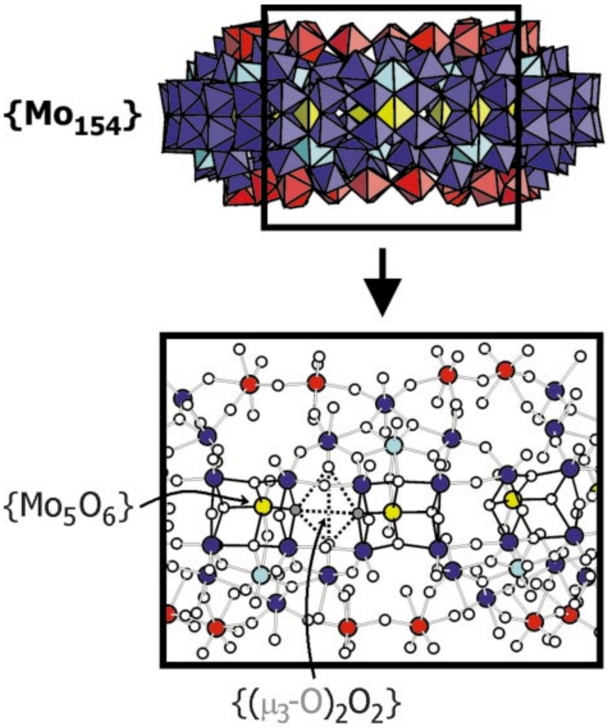


Fig. 8 Polyhedral representation of the tetradecameric $\{Mo_{154}\}$-type cluster with view perpendicular to that depicted in Fig. 7 (*top*) and structural details of cluster compartments in ball-and-stick representation (*bottom*). This representation highlights (1) three of the 14 (incomplete) double-cubane-type compartments each of which is spanned by five Mo centers (Mo–Mo = 3.4–4.0 Å) belonging to $\{Mo_8\}$- as well as $\{Mo_1\}$-type groups and six O atoms (the lowered bond valence sum (BVS) values of the corresponding Mo atoms with an average value of 5.6 prove, besides other experimental data, that two 4d electrons are trapped in each compartment), and (2) one of the 14 $\{(\mu_3\text{-}O)_2O_2\}$-type compartments indicated by dotted lines which are located between two double-cubane-type compartments (the two characteristic μ_3-O atoms (dark grey, O–O = 3.07 Å) have an average BVS value of 1.2 indicating a degree of protonation; for details see ref. 34). ($\{Mo_8\}$: blue (central MoO_7 pentagonal bipyramid: cyan), $\{Mo_1\}$: yellow, $\{Mo_2\}$: red).

The use of the above-mentioned fundamental *linkable building units*, *e.g.* in the form of Platonic solids, enables the generation of molecular systems of higher structural variability and versatility compared to arrangements of aggregated metal atoms with spherical symmetry, which lead to pure metal clusters or ligand-stabilized clusters with metal cores. In the present case, the final macroscopic product is the crystalline metal oxide, in the latter, the crystalline metal. Important research in this area has been done by Schmid.[15]

The basic principles of the *one-pot reactions*, mainly those with feedback effects, non-linearity relations and induced cascades (see below), are of relevance for fundamental problems of prebiotic chemistry and conservative self-organization in general. *This is especially valid in the present case with reference to the combinatorially linkable (virtual) units as disposition*. The prebiotic situation is very well reflected by a citation from *Scientific American* that deals with the work of a well-known member of the Santa Fe institute:

> “[Stuart A.] Kauffman’s simulations have led him to several conclusions. One is that when a system of simple chemicals reaches a certain level of complexity [...], it undergoes a dramatic transition, or phase change. The molecules begin spontaneously combining to create larger molecules of increasing complexity and catalytic capability. Kauffman has argued that this process of ‘autocatalysis’—rather than the fortuitous formation of a molecule with the ability to replicate and evolve–led to life.” [16]

On the other hand, one-pot reactions are, in principle, of industrial interest according to Dömling and Ugi’s MCR (multi-component reaction)-type studies.[17]

Aspects of self-aggregation, related reaction types and synthesis

Preventing degradation as well as uncontrolled aggregation

The most suitable strategy to guarantee limited growth as well as synthetic aspects in the present case of polyoxometalate chemistry is based on the generation of sufficiently negatively charged fragments (intermediates formed during the aggregation process) enabling growth by avoiding both a possible degradation due to hydrolysis and an uncontrolled aggregation to network-type structures, leading for instance to the formation of the related oxides. This can be attained not only by substituting some metal centers of lower for ones of higher oxidation state or by substituting less positively charged for higher positively charged groups (*e.g.* by exchanging $[Mo(NO)]^{3+}$ for $[MoO]^{4+}$), but also by the (permanent) presence of an appropriate reducing agent or even different types of these. It is of utmost importance to keep the growing molecular system in solution, which can be achieved by avoiding a too high nucleophilicity of the peripheral oxygen atoms, thus preventing aggregation. This is accomplished for instance by the presence of a large number of H_2O ligands which cause the high solubility in protic media and/or terminal doubly bonded oxygen atoms of the O=Mo groups.

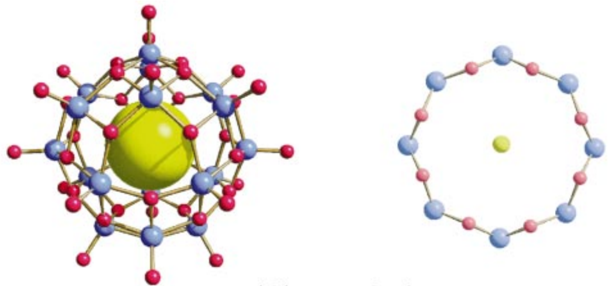
In the reaction system MoO_4^{2-}–H_2O–NH_2OH–$(X^VO_4^{3-})$ highly negatively charged species are abundant, for instance the highly soluble ion $[Mo^{VI}_8V^{IV}_4O_{36}(X^VO_4)]^{11-}$ (X = V; As; without protonation); the latter species can be trapped with electrophiles such as the As^{III} centers, resulting in the less soluble stable cluster species $[As^{III}_2Mo^{VI}_8V^{IV}_4O_{36}(As^VO_4)]^{5-}$ with lowered negative charge.[11c,e] Other negatively charged linkable (virtual) fragments as disposition, such as the $\{Mo_{17}\}$ unit which can be ‘linked’ in different ways by certain electrophilic metal centers (or linkers) such as Fe^{III} or $V^{IV}O^{2+}$, form larger systems, *e.g.* the three-fragment cluster of the $\{Mo_{57}M_6\}$ type with three $\{Mo_{17}\}$ units. A higher nucleophilicity of the fragments and a higher coordination number of the linkers can lead to giant species with a larger number of linked fragments (for the remarkable giant tungstate-based cluster of Pope and coworkers see below).

Spectroscopic detection of stability regions and conditions for further aggregation

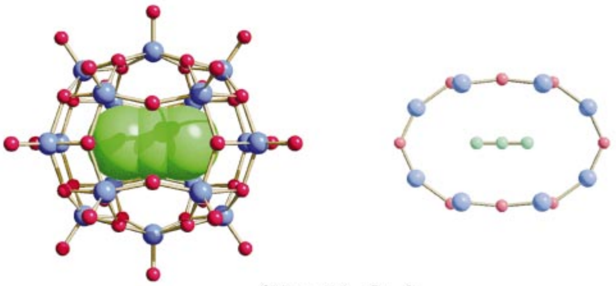
The possibility of spectroscopic detection of the mentioned clusters in solution (*e.g.* by means of resonance-Raman spectroscopy) constitutes a good *base when studying conditions for the generation of ever larger species. Stability regions of the clusters can be determined and further possible aggregation processes under different conditions can be recognized upon changing the pH values and redox potentials*. Starting for instance with the above mentioned two-fragment $\{Mo_{36}\}$-type cluster with two $\{Mo_{17}\}$ groups, the three-fragment $\{Mo_{57}M_6\}$-type cluster with three $\{Mo_{17}\}$ groups is formed after adding for instance the strong electrophilic linker $V^{IV}O^{2+}$ under reducing conditions. In solutions containing this cluster, the (more reduced) wheel-shaped cluster $[Mo_{154}(NO)_{14}O_{448}H_{14}(H_2O)_{70}]^{28-}$ ($\{Mo_{154}\}$) forms upon further acidification and reduction ($\{Mo_{154}\}$-type clusters like the pure isopolyoxometalate analogue containing 14 $[MoO]^{4+}$ instead of 14 $[MoNO]^{3+}$ groups turned out to comprise the prototype of the molybdenum-blue species).[18] These clusters can be regarded as tetradecamers that meet D_{7d} symmetry if the hydrogen atoms are excluded and can be formally generated by linking 140 MoO_6 octahedra and 14 $MoO_6(NO)$ or MoO_7 pentagonal bipyramids, forming the building blocks of the $\{Mo_8\}$, $\{Mo_2\}$, and $\{Mo_1\}$ type which are each present in the tetradecameric cluster type 14 times.

Template-driven aggregation: an example

An important strategy often used is that of template-controlled linking especially of relatively small building units (for a review see ref. 19 but also ref. 20). It is for instance possible to link square pyramids built up by five oxygen atoms and a central vanadium atom to form cage systems. The resulting cage, *i.e.* the cluster shell, is formed complementary to the size and shape of the template which is finally encapsulated as guest in the reaction product. The relevant condensation process is initiated by adding negatively charged template ions to an aqueous solution containing vanadate ions in presence of a reducing agent which leads to the formation of polyoxovanadates (IV) or mixed-valent polyoxovanadates (IV,V). A spherically shaped halogenide anion (*e.g.* Cl^-) as template induces the formation of a spherically shaped cage, whereas the presence of the elongated azide anion results in an elongated (stretched) cluster cage (Fig. 9).[19,20] This procedure can also be regarded formally as a 'slaving' process according to Haken's concept of synergetics:[21] the template 'forces' or 'slaves' the square-pyramidal units to get aggregated in a uniform way. The analogy of the relevant host–guest system, in which the metal–oxygen cluster cage can be regarded as host and the enclosed anion as guest, to the endohedral fullerenes is evident (where in fact metal cations are present as guests). It should be noted that the interaction of the cluster shell with the anion is very weak (but cation stabilized) and consequently the cluster shells may be used as matrices for quasi-isolated anions.[22]



$\{Cl^- \subset V_{18}O_{42}\}$

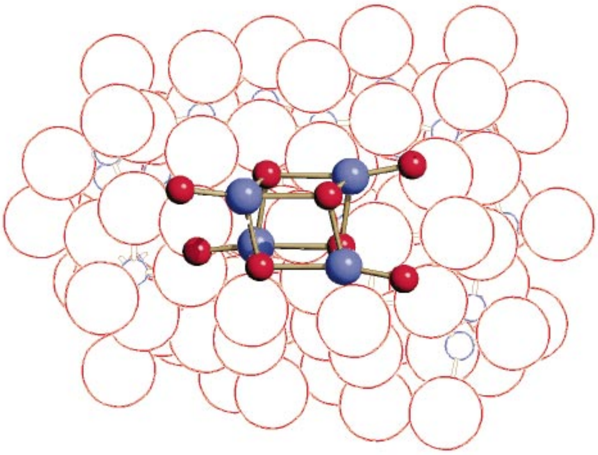


$\{N_3^- \subset V_{18}O_{44}\}$

Fig. 9 Representation of the complementarity of the polyoxovanadate shell (host) formed by linking OVO_4 square pyramids (archetypical for the formation of relevant parts of concave host structures) and the encapsulated convex anion (guest) directing the linking as a template.

It is furthermore remarkable that all known resulting cluster shells can be regarded as sections of layers of vanadium pentoxide (V_2O_5).[19a,23] (The curvature of the cluster shell is due to the negative partial charges at the peripheral oxygen atoms.) This means that one can describe the cluster cages as being formally cut out from the layers of a crystalline compound.

Of particular interest is the case of *a template, generated in solution in an initial step, directing or determining the subsequent linking processes*: a cubane-type $\{V_4O_4(O_{term})_4\}$ fragment with the stoichiometry of amphoteric $V^{IV}O_2$, obviously primarily formed in solution, induces the formation of a cluster the structure of which has similarity with a segment of the (cubic) NaCl defect structure (Fig. 10).[24]



$\{V_{34}\}$

Fig. 10 Structure of the cluster anion $[V_{34}O_{82}]^{10-}$ with the highlighted $\{V_4O_4(O_{term})_4\}$ cubane-type central unit (formed initially in the reaction solution) acting formally as template, as in the case of the clusters of Fig. 9. The $\{V_{34}\}$-type cluster has similarity with a segment of the (cubic) NaCl defect structure (the 'shell' framework in space-filling, the central unit in ball-and-stick representation).

Molecular growth to complexity *via* an induced cascade

During natural evolution the emergence of more complex molecular structures from simpler ones occurred. In this context, basic principles of induced cascade reactions of the type given in Scheme 1 are of special relevance:

$$\begin{tikzcd}
\mathbf{I} \arrow[r, Rightarrow] \arrow[dr] & \mathbf{III} \arrow[r, Rightarrow] \arrow[dr] & \mathbf{V} \arrow[r, Rightarrow] \arrow[dr] & \mathbf{VII} & (2N\text{–}1) \\
 & \mathbf{2} \arrow[u, Rightarrow] & \mathbf{4} \arrow[u, Rightarrow] & \mathbf{6} \arrow[u, Rightarrow] & (2n)
\end{tikzcd}$$

Scheme 1

The odd Roman numerals $2N - 1$ signify maturation steps of a molecular system in growth or development and the Arabic numerals $2n$ represent 'reagents' that react only with the special preliminary intermediate $2N - 1$. The 'species' $2n$ can themselves be products of self-assembly processes, but can remarkably be generated template-driven by the corresponding intermediate $2N - 1$. *In the latter case each intermediate* $2N - 1$ *carries information inducing the formation of the subsequent intermediate* $2n$ *(induced cascade-type reaction)* with which it then reacts thus demonstrating an interesting feedback effect.

One example for a growth process according to this model scheme has been investigated in detail: a cluster anion containing 37 molybdenum atoms ($[H_{14}Mo_{37}O_{112}]^{14-}$) is formed *via* intermediates,[25] one of which, the cluster of the type $\{Mo^{V}_{12}Mo^{VI}_{4}\}$ (containing an ε-Keggin-type nucleus capped by four electrophilic $\{Mo^{VI}O_3\}$ groups), can be isolated from the reaction medium[26a] (this $\{Mo_{16}\}$ fragment also resembles the core of other larger clusters with higher symmetry, such as $[XH_nMo_{42}O_{109}\{(OCH_2)_3CR\}_7]^{m-}$ with $X = Na(H_2O)_3^+$: $n = 13, m = 9$; $n = 15, m = 7$ or $X = MoO_3$: $n = 14, m = 9$; $n = 13, m = 10$).[26b] After the relevant reduction of the four surface constituents of the type $\{Mo^{VI}O_3\} \rightarrow \{Mo^{V}O_3\}$, the intermediate cluster acts both as nucleophile *and* template in directing the formation of two further electrophilic molybdenum-oxide based intermediates ($\{Mo_{10}\}$ and $\{Mo_{11}\}$). These subsequently react with their template (in a type of symmetry-breaking step) leading finally to the reaction product, the $\{Mo_{37}\}$-type cluster which remarkably has no (higher) symmetry element (Fig. 11). The most interesting aspect is that the former electrophilic $\{Mo^{VI}O_3\}$ groups are transformed into nucleophilic $\{Mo^{V}O_3\}$ ones after they have been attached to the cluster surface. The reduction of units on the cluster surface seems to be (1) the basis of the growth processes investigated here (as the growing system always has a nucleophilic surface)

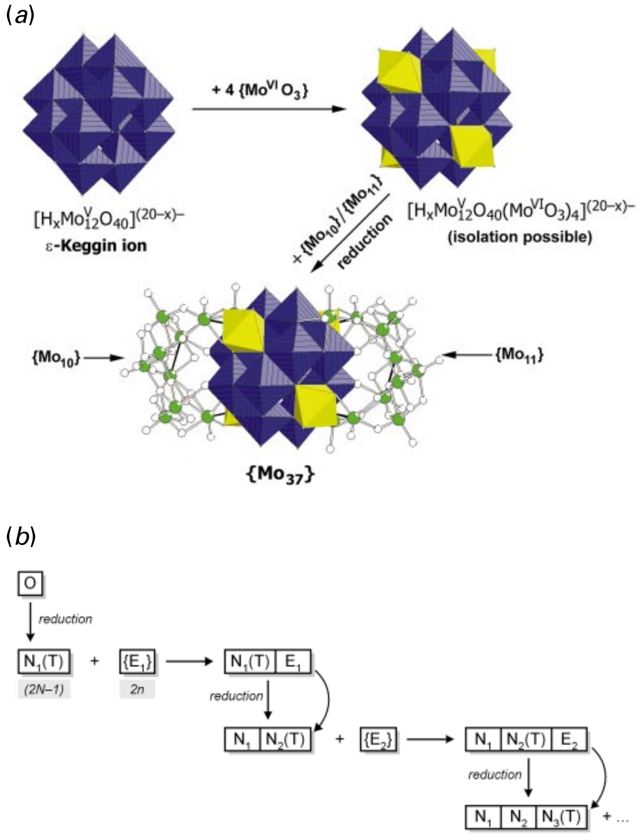


Fig. 11 (*a*) Schematic representation of a molecular growth process based on an induced cascade and molecular symmetry-breaking steps according to the reaction Scheme 1 (see text); the resulting $\{Mo_{37}\}$ cluster remarkably does not show any (higher) symmetry elements. (*b*) Reaction scheme corresponding to the growth process shown in (*a*), demonstrating principally the step-by-step procedure in which nucleophiles (such as the reduced ε-Keggin ion) attract electrophiles (such as $\{Mo^{VI}O_3\}$). Remarkably these can become nucleophiles ($\{Mo^{V}O_3\}$ units) on the surface of the cluster upon reduction. O denotes species at the beginning of a growth process (formally the non-reduced ε-Keggin ion). $N_i(T)$ denotes a nucleophilic intermediate/fragment produced under reducing conditions (of the type $2N - 1$ according to Scheme 1, *e.g.* the reduced ε-Keggin ion) with a potential template function for the generation of the electrophilic intermediate E_i (of the type $2n$ according to Scheme 1, *e.g.* the $\{Mo^{VI}O_3\}$ groups).

and (2) the entering point into the world of open systems, since the reduction of the $\{Mo^{VI}O_3\}$ groups at the surface of the cluster can in principle be performed ‘externally’ by adding an appropriate reducing agent at the right time. It is important to note that these types of integrated constituents (here situated on the surface of a cluster) are more easily reduced than the discrete ones.

Large clusters and the correlated size(form)/complexity(functionality) pair

An increase in the size of a molecular system can *in principle* lead to multi-functionality whereby with increasing size of the system the correlated concept pair, form–function, can correspondingly become more and more important. This should be elucidated by the following examples:

(1) In the case of the mentioned $\{Mo_{57}M_6\}$-type cluster, it is possible to *place* (*or exchange*) *step-wise different* (*para*)-*magnetic centers* M *like* $Fe^{II/III}$ *and* $V^{IV}O^{2+}$ *in the respective linker positions*, thus allowing some control over the cluster’s magnetic properties or even the tuning of these.[27] On the other hand the cluster in question exhibits cavities on its periphery. This is of special interest since these *cavities can be filled with positively charged units such as* $[MoO]^{4+}$ *under reducing conditions* (*i.e.* by increasing the nucleophilicity) *and can be emptied again upon oxidation* (Fig. 12). As mentioned earlier,

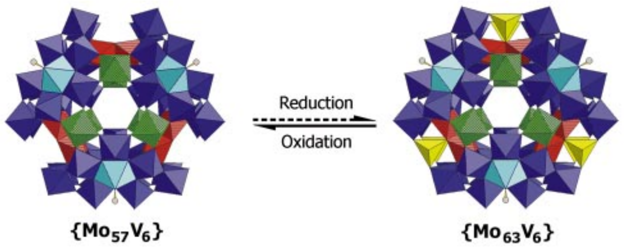


Fig. 12 Quasi-reversible molecular growth $\{Mo_{57}M_6\} \longrightarrow \{Mo_{63}M_6\}$ based on a type of switchable sites: six electrophilic $[MoO]^{4+}$ groups (yellow tetrahedra) can (formally) be taken up step-wise under reducing conditions (by the nucleophilic cluster) to form finally the $\{Mo_{63}M_6\}$ cluster, but can be expelled when the latter cluster is oxidized (see text).

this seems to be the basic principle of the growth processes under consideration: aggregation or growth is due to interaction of nucleophilic growing species with electrophilic groups. The reaction, based on a kind of switchable sites, represents a type of model for uptake and release of metal centers in metal storage proteins under redox-active conditions.[25]

(2) A further nice example is presented by the cluster anion $\{Mo_{75}V_{20}\}$.[28] Interestingly, virtual $\{(Mo)Mo_5\}$ pentagons (as disposition) in solutions can be used as basic building blocks in presence of other building blocks to construct spherical species, *e.g.* derivatives of the $\{Mo_{132}\}$-type cluster with its 12 pentagonal $\{(Mo)Mo_5\}$ units. This leads for instance to the mentioned cluster anion which can be described with reference to one of the Archimedean solids, namely the icosidodecahedron with 30 corners and 32 faces. This Archimedean solid is formed by 12 pentagonal and 20 triangular faces built up by 20 V^{IV} and 10 Mo^{VI} centers while ten pentagonal faces of the icosidodecahedron are capped by the $\{(Mo)Mo_5\}$ pentagons (Fig. 13, 14). Besides the remarkable fact that the ten triangles, built up by the 20 V^{IV} centers, form an equatorial paramagnetic ring-shaped band with very strong antiferromagnetic exchange interactions, the cluster opens the doorway for new aspects of supramolecular chemistry because of the abundance of two $\{(NaSO_4)_5\}$-type rings inside the cavity. On the other hand it seems to be clear that the $V^{IV}O^{2+}$ groups should in principle be replaceable by Fe^{III} centers (as in the case of the $\{Mo_{57}M_6\}$-type cluster), which could enable a tuning of magnetic properties. In particular it could result in an isolation of clusters

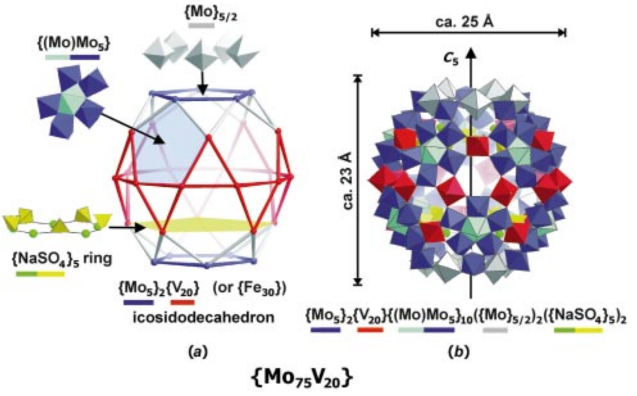


Fig. 13 (*a*) $\{V_{20}Mo_{10}\}$ framework structure of the $\{Mo_{75}V_{20}\}$-type cluster with 30 corners and 32 faces (20 triangles and 12 pentagons) spanned by 20 V^{IV} (red) and 10 Mo^{VI} (blue) centers (the Fe atoms of the related $\{Fe_{30}\}\{(Mo)Mo_5\}_{12}$-type cluster form a less distorted icosidodecahedron). Additional details: (1) one of the $\{(Mo)Mo_5\}$ units capping 10 pentagonal faces (Mo pentagonal bipyramid: light blue, Mo octahedra: dark blue), (2) pentagonal (under-occupied) array built up by the five MoO_6 octahedra capping the other two pentagonal faces (grey), (3) a ‘magnetic’ ring-shaped band formed by 10 $V^{IV}{}_3$ triangles having common corners (red) and (4) one of the two encapsulated $\{NaSO_4\}_5$-type rings (Na atoms: green, SO_4 tetrahedra: yellow). (*b*) Polyhedral representation of the (approximately) spherical structure of the complete $\{Mo_{75}V_{20}\}$-type cluster.

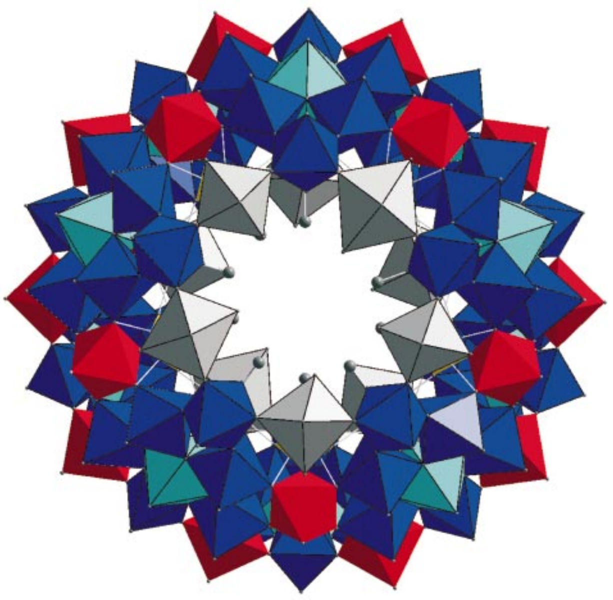


Fig. 14 Polyhedral representation of the $\{Mo_{75}V_{20}\}$-type cluster with a view along the C_5 axis, *i.e.* perpendicular to that depicted in Fig. 13(*b*) (colour code as in Fig. 13).

with an icosidodecahedral base spanned by 30 Fe centers. This for instance would correspond to a derivative of the $\{Mo_{132}\}$ cluster having also 12 $\{(Mo)Mo_5\}$ pentagons but the 30 $\{Mo^{V}{}_2O_4\}^{2+}$ groups replaced by 30 Fe^{III} centers.

(3) The *size/multi-functionality* concept pair can be elucidated very well by means of the giant wheel-type cluster, *e.g.* the tetradecameric $\{Mo_{154}\}$-type cluster and its properties:

1. It exhibits a nanometer-sized cavity, presenting new perspectives for a novel host–guest chemistry.
2. It has an extended hydrophilic inner and outer surface owing to the presence of 70 H_2O ligands.
3. It has a huge surface area which explains in part the high affinity towards adsorbents, such as charcoal or silk.
4. It renders a molecular model for catalytically active metal oxides.
5. The aqueous solution shows further aggregation tendencies: the formation of colloids of 40 nm hydrodynamic radius could be detected by means of dynamic light scattering and scanning electron microscopy.[29]
6. The periphery of the cluster ring shows a rather high electron density.
7. There are 14 uncoupled $\{Mo_5O_6\}$ (incomplete double-cubane) compartments, each of which carries two delocalized 4d electrons (comparable to a so-called electronic necklace, *i.e.* corresponding to an electron-storage system where the uncoupled storage elements are threaded like pearls on a string).[34]
8. It is possible to generate deliberately discrete structural defects on the inner surface of the cluster ring by abstracting positively charged $\{Mo_2\}$ groups using special ligands which have a high affinity to these groups (see below).
9. The ring-shaped units can be linked according to a type of crystal engineering: assembly owing to synergetically induced functional complementarity of distinct surface sites (see below).
10. It is possible to place molecules or replace ligands at different sites of the surface (thereby subsequently changing the properties) and to study direct reactions between the molecules placed inside the cavity.

Relevant compounds containing the ring-shaped units are presented in Table 1.

Table 1 Compounds with nanosized rings: building units (Fig. 8) and bond valence sum values relating to the structures[a]

Compound (with approximate crystal water content)[a]	Building units[b]	Structure	BVS[c] (Mo)	BVS[d] (μ_3-O)	Ref.
$(NH_4)_{28}[Mo_{154}(NO)_{14}O_{448}H_{14}(H_2O)_{70}]\cdot xH_2O$ ($x \approx 350$)	$\{Mo_2\}_{14}\{Mo_8\}_{14}\{Mo_1\}_{14}$	Discrete rings	5.7	1.2	13
$Na_{14}[Mo_{154}O_{462}H_{14}(MeOH)_8(H_2O)_{62}]\cdot xH_2O\cdot yMeOH$[e] ($x \approx 400$, $y \approx 10$)	$\{Mo_2\}_{14}\{Mo_8\}_{14}\{Mo_1\}_{14}$	Discrete rings	5.5	1.2	30
$Na_{15}\{0.5[Mo_{154}O_{462}H_{14}(H_2O)_{70}]\cdot 0.5[Mo_{152}O_{457}H_{14}(H_2O)_{68}]\}\cdot xH_2O$ ($x \approx 400$)	$\{Mo_2\}_{14}\{Mo_8\}_{14}\{Mo_1\}_{14}$ + $\{Mo_2\}_{13}\{Mo_8\}_{14}\{Mo_1\}_{14}$	Two different discrete rings, one of which possesses a defect	5.6 5.6	1.2 1.2	31
$Li_{16}[Mo_{176}O_{528}H_{16}(H_2O)_{80}]\cdot xH_2O$($x \approx 400$)	$\{Mo_2\}_{16}\{Mo_8\}_{16}\{Mo_1\}_{16}$	Discrete rings	5.6	1.3	32
$Na_{16}[Mo_{176}O_{528}H_{16}(MeOH)_{17}(H_2O)_{63}]\cdot xH_2O\cdot yMeOH$ ($x \approx 600$, $y \approx 30$)	$\{Mo_2\}_{16}\{Mo_8\}_{16}\{Mo_1\}_{16}$	Discrete rings	5.7	1.3	33
$Na_{24}\{0.5[Mo_{144}O_{437}H_{14}(H_2O)_{56}]\cdot 0.5[Mo_{144}O_{437}H_{14}(H_2O)_{60}]\}\cdot xH_2O$ ($x \approx 350$)	$\{Mo_2\}_9\{Mo_8\}_{14}\{Mo_1\}_{14}$ + $\{Mo_2\}_9\{Mo_8\}_{14}\{Mo_1\}_{14}$	Discrete rings with defects and chains built up by rings with defects	—[f]	—[f]	34
$Na_{24}[Mo_{144}O_{437}H_{14}(H_2O)_{56}]\cdot xH_2O$ ($x \approx 250$)	$\{Mo_2\}_9\{Mo_8\}_{14}\{Mo_1\}_{14}$	Chains built up by rings with defects	5.8	1.2	35
$Na_{22}[Mo_{146}O_{442}H_{14}(H_2O)_{58}]\cdot xH_2O$ ($x \approx 250$)	$\{Mo_2\}_{10}\{Mo_8\}_{14}\{Mo_1\}_{14}$	Chains built up by rings with defects	5.6	1.2	31
$Na_{16}[Mo_{152}O_{457}H_{14}(H_2O)_{66.5}]\cdot xH_2O$ ($x \approx 300$)	$\{Mo_2\}_{13}\{Mo_8\}_{14}\{Mo_1\}_{14}$	Layers built up by rings with defects	5.6	1.2	34
$Na_{21}[Mo_{154}O_{462}H_{14}(H_2O)_{54}(H_2PO_2)_7]\cdot xH_2O$ ($x \approx 300$)	$\{Mo_2\}_{14}\{Mo_8\}_{14}\{Mo_1\}_{14}$	Layers with attached $H_2PO_2^-$ groups	5.6	1.2	36

[a] Formulae of some earlier reported compounds corrected according to the now accepted type of protonation for compounds with $b = 14$ building units (tetradecameric case) or $b = 16$ (hexadecameric case). [b] The general formula for the discrete pure molybdenum–oxide based unit is $[\{Mo^{VI}{}_2O_5(H_2O)_2\}^{2+}{}_{b-x}\{(Mo^{VI/V}{}_8O_{26}(\mu_3\text{-}O)_2H_m(H_2O)_3Mo^{VI/V})^{(4-m)-}\}_b]^{(2b-bm+2x)-} \equiv [\{Mo_2\}_{b-x}\{Mo_8\}_b\{Mo_1\}_b]^{(2b-bm+2x)-}$ [b = number of building units per set = number of compartments referring to Fig. 8 = number of protonations at the equatorial μ_3-O atoms or in the $\{(\mu_3\text{-}O)_2O_2\}$ compartment (for $m = 1$) = half of the (formal) number of Mo^V centers; x = number of defects or missing $\{Mo_2\}^{2+}$ units]. [c] Average BVS value for the Mo centers which span the b incomplete $\{Mo_5O_6\}$-type double cubanes, built up by (parts of) the $\{Mo_8\}$ and $\{Mo_1\}$ units (Fig. 8). The (formal) number of Mo^V centers per ring is for all compounds $2b$ (or two per compartment) according to the related constant BVS (Mo) values and other experimental data (see text). [d] Average BVS value for the μ_3-O atoms of the $b = 14$ or 16 $\{(\mu_3\text{-}O)_2O_2\}$-type compartments (Fig. 8), which indicates protonation at the equatorial μ_3-O atoms or within the $\{(\mu_3\text{-}O)_2O_2\}$compartments. The finally accepted value for the number of protons m per compartment is 1 mainly according to the results of the numerous cation analyses. This value corresponds to a disorder of the kind that only one of the two μ_3-O atoms of a compartment is protonated. This situation ($m = 1$) is also more plausible as the other possibility ($m = 2$) leads to a rather small H–H distance in the compartment (compare W. H. Baur, *Acta Crystallogr., Sect. B*, 1992, **48**, 745). [e] Because of the rather high resolution of the crystal structure, Na^+ positions could be determined for the first time, proving their importance for the structure formation. [f] The structure is not sufficiently resolved to calculate reasonable BVS values.

On route to larger and more complex systems: supramolecular and solid-state structures

An aspect of particular interest is the fact that the large ring-shaped synthons can assemble to form chains or layers (Table 1).[34–36] The assembly is based on the replacement of H_2O ligands at $\{Mo_2\}$ units (on rings) by oxygen atoms of terminal Mo=O groups (on other rings), the nucleophilicity of which is increased for instance by introducing electron donating (and the linking-introducing) ligands like $H_2PO_2^-$ at relevant neighbouring sites (Fig. 15). In this case a *layer compound* can be obtained.[36] In addition, as the process is based on reactions at the same type of amphiphilic $\{Mo_2\}$-type O=MoL (L = H_2O, $H_2PO_2^-$) units in different rings, the term synergetically induced functional complementarity seems to be justified. The hypophosphoric acid in this case acts both as reducing agent and H_2O-replacing ligand. Linking is in principle also possible by abstracting some $\{Mo_2\}$-type fragments using bidentate ligands, such as the formate anion, from the inner surroundings of the $\{Mo_{154}\}$-type cluster which also causes a higher nucleophilicity at the O=Mo(H_2O) sites of $\{Mo_2\}$ units in the neighbourhood. *Compounds with chains* having interesting electronic properties can be formed in this way (see Fig. 16 and Table 1).[31,34]

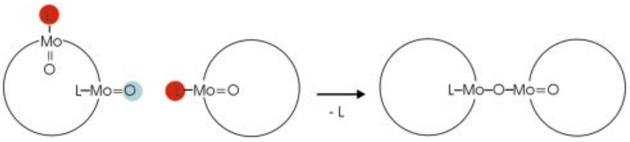


Fig. 15 Schematic representation of the basic assembly principles of ring-shaped cluster units forming the layers with $[Mo^{VI}_{126}Mo^{V}_{28}O_{462}H_{14}(H_2O)_{54}(H_2PO_2)_7]^{21-}$ units. The formation is based on the synergetically induced functional complementarity of the $\{Mo_2\}$-type O=Mo(L) (L = H_2O, $H_2PO_2^-$) sites of their surfaces: each precursor ring contains the corresponding virtual functional complementary O=Mo(H_2O) groups (becoming 'donors' due to the electron-donating $H_2PO_2^-$ replacing H_2O ligands and 'acceptors' without $H_2PO_2^-$ ligands).

An even larger ring-shaped cluster than the tetradecameric $\{Mo_{154}\}$ type with 176 molybdenum atoms ($\{Mo_{176}\}$), *i.e.* with a hexadecameric structure, can be obtained containing correspondingly 16 instead of 14 sets of each of the three mentioned building blocks of the type $\{Mo_8\}$, $\{Mo_2\}$ and $\{Mo_1\}$ (Fig. 17, Table 1).[32,33] Under special reducing conditions the cluster system even starts growing again while two molybdenum–oxide fragments of the type $\{Mo_{36}O_{96}(H_2O)_{24}\}$ cover the cavity of the wheel-shaped cluster like hub-caps, resulting in an $\{Mo_{248}\}$-type cluster (Fig. 18).[37] This is in terms of the number of metal atoms the largest known cluster anion that has been structurally characterized so far. Remarkably the structure of the $\{Mo_{36}O_{96}(H_2O)_{24}\}$-type fragment is nearly identical to a segment of the solid-state structure of the compound Mo_5O_{14} (Fig.19).[38] This offers the possibility to model crystal growth under boundary conditions, especially the related initial nucleation process which is not understood at all. On the other hand,

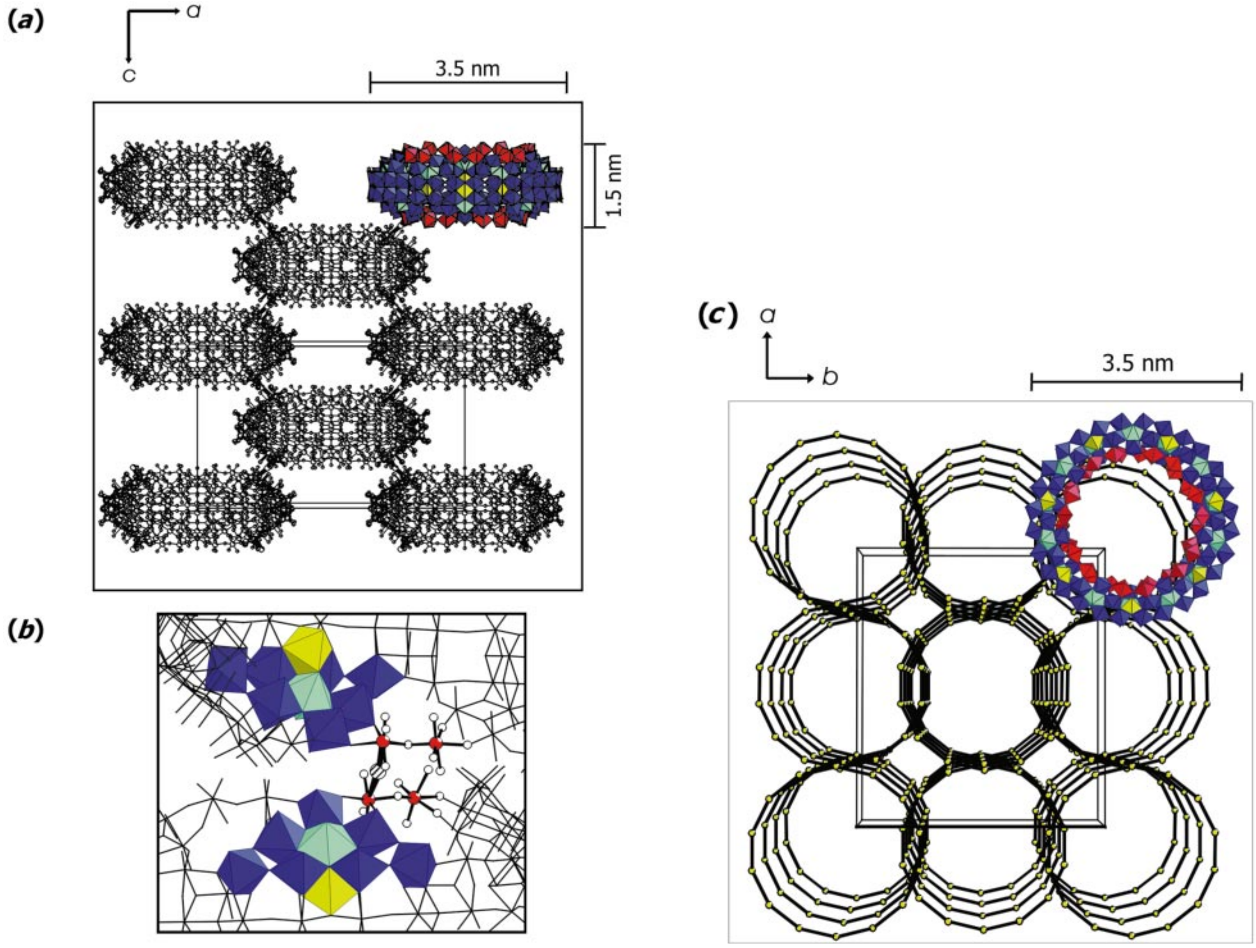


Fig. 16 (*a*) Ball-and-stick representation of the 'packing' of the covalently (in direction of the *b* axis) linked rings in crystals of $Na_{16}[Mo^{VI}_{124}Mo^{V}_{28}O_{429}(\mu_3\text{-}O)_{28}H_{14}(H_2O)_{66.5}]\cdot xH_2O$ ($x \approx 300$) ($\{Mo_{152}\}$) viewed along the crystallographic *b* axis. Each ring is connected to surrounding rings *via* Mo–O–Mo bridges of the O=Mo–O–Mo–OH_2 units, thus forming layer networks parallel to the *ac* plane. One ring is shown as basic unit in polyhedral representation ($\{Mo_2\}$ units: red, $\{Mo_8\}$: blue (central MoO_7 pentagonal bipyramid: cyan), $\{Mo_1\}$: yellow). (*b*) Detailed view of the bridging region between two cluster rings. One $\{Mo_8\}$ unit of each ring together with one $\{Mo_1\}$ unit is shown in polyhedral representation and one $\{Mo_2\}^{2+}$ (= $\{Mo^{VI}_2O_5(H_2O)_2\}^{2+}$) unit per ring in ball-and-stick representation (Mo centers: red). The bridging (disordered) oxygen centers are depicted as large, hatched circles (for clarity, the disorder in the bridging positions is not shown here). (*c*) Perspective view along the crystallographic *c* axis showing the framework with nanotubes which are filled with H_2O molecules and Na^+ cations. For clarity, only one ring is shown completely in polyhedral representation. For the other rings only the centers of the $\{Mo_1\}$ units (yellow) are given and connected. The diameter of the central cavity inside a ring in the crystal is at least 1.9 nm.

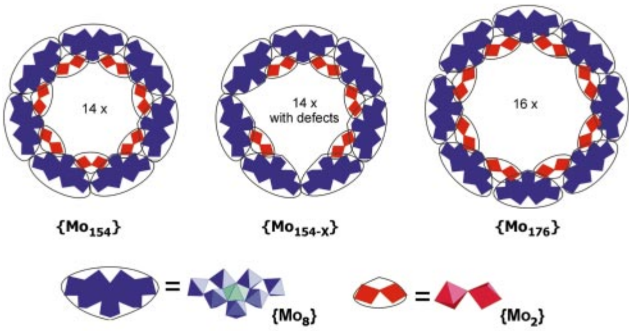


Fig. 17 Schematic comparison of the tetradecameric $\{Mo_{154}\}$- (with and without defects referring to missing $\{Mo_2\}$ groups) and hexadecameric $\{Mo_{176}\}$-type cluster showing the basic $\{Mo_8\}$ and $\{Mo_2\}$ units (the equatorial $\{Mo_1\}$ units are not visible in this representation).

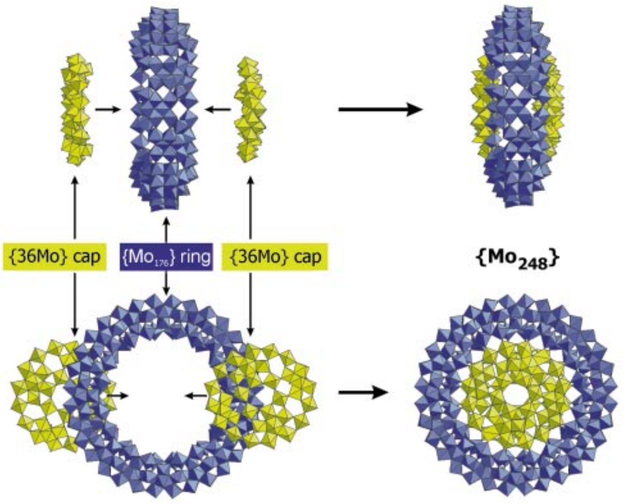


Fig. 18 Schematic representation of the growth process $\{Mo_{176}\} \rightarrow \{Mo_{248}\}$. The structure of one $\{Mo_{248}\}$ cluster can formally be decomposed into one $\{Mo_{176}\}$-type ring (blue) and two $\{Mo_{36}O_{96}(H_2O)_{24}\}$-type hub-caps (yellow).

this type of aggregation has relevance for metal-center assembly in biological systems, in particular in the case of special types of biomineralization in compartments.

In this context important work on large inorganic cluster systems based on copper selenide (*e.g.* $[Cu_{146}Se_{73}(PPh_3)_{30}]$),[39a] silver selenide (*e.g.* $[Ag_{172}Se_{40}(SeBu^n)_{92}(dppp)_4]$),[39b] metal cores (*e.g.* $[Al_{77}\{N(SiMe_3)_2\}_{20}]^{2-}$)[40] and polyoxotungstate systems (*e.g.* $[As_{12}Ce_{16}(H_2O)_{36}W_{148}O_{524}]^{76-}$)[41] should be mentioned, too.

The ring-shaped $\{Mo_{154}\}$-type clusters linked to chains can also act as hosts for smaller polyoxometalate guests, such as the (non-reduced) two-fragment $\{Mo_{36}\}$-type cluster.[42] In this novel supramolecular system the interaction between host and guest, which fits exactly into the cavity of the host, is due to 16 hydrogen bonds as well as the Coulomb interaction mediated by four sodium cations located between the negatively charged host and negatively charged guest (Fig. 20).

Facile and high-yield synthesis of the considered compounds with giant cluster anions

The precipitation and isolation of some of the giant cluster anions, mainly those with high solubility, caused difficulties for generations of chemists in the past, but also during the initial phase of our related investigations. Generations of chemists have for instance tried, without success, to isolate pure compounds or even a few crystals (only amorphous material obtained) from molybdenum blue solutions. These contain *e.g.* highly soluble giant cluster anions of the $\{Mo_{154}\}$ type which can be formed by reducing agents from molybdate solutions within minutes.[18,31] In the meantime, we have solved this problem: in the presence of a high electrolyte concentration (method of choice) the solubility is tremendously reduced so that the discrete $\{Mo_{154}\}$- and $\{Mo_{176}\}$-type clusters[30,31,33] and also related compounds with chain[31] and layer[36] structures could be obtained in a high-yield within a short time and in pure crystalline form. The same is valid for the $\{Mo_{132}\}$-Keplerate-type compound which can be obtained as very large crystals for which the precipitation is not problematical.

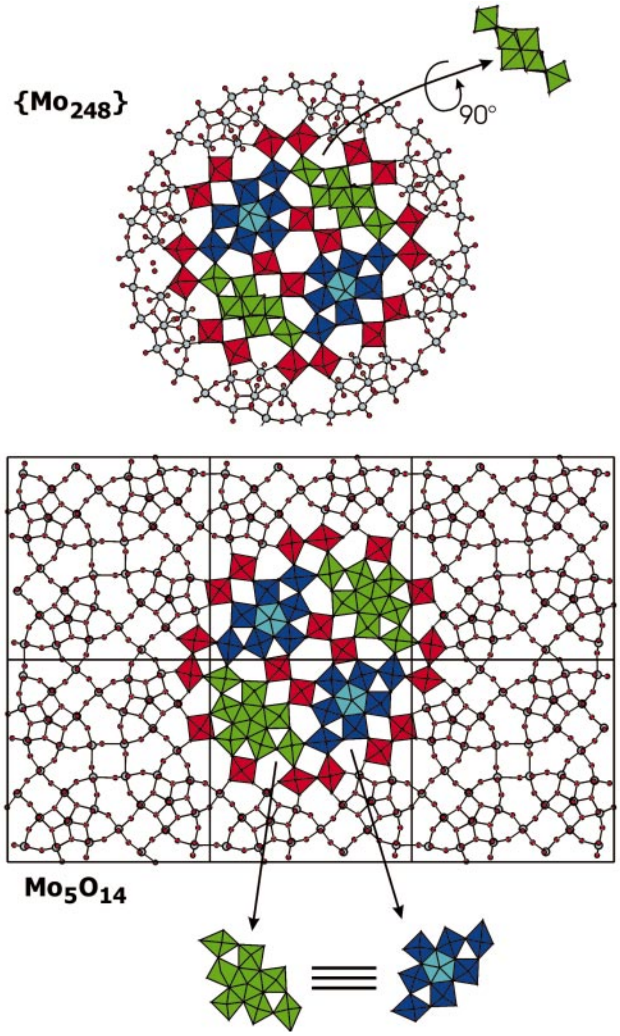


Fig. 19 Structural comparison of the hub-cap motif of the $\{Mo_{248}\}$ cluster and the related segment of the solid-state structure of Mo_5O_{14}. *Above*: schematic representation of one half of the $\{Mo_{248}\}$ cluster with a highlighted $\{Mo_{36}O_{96}(H_2O)_{24}\}$ hub-cap in polyhedral representation. *Below*: structure of Mo_5O_{14} viewed along the *c* axis [see ref. 38(*a*) for details]. Both the hub-caps and the Mo_5O_{14} layer sections each contain four $\{Mo_8\}$ entities surrounding two central $\{Mo_2\}$ units. A central ring of six MoO_6 octahedra is formed by these two $\{Mo_2\}$ units and two MoO_6 octahedra belonging to two opposite $\{Mo_8\}$ entities. Whereas in the case of the Mo_5O_{14} layer section the four $\{Mo_8\}$ entities (two blue; two green) are of the 'usual' type and occur in several of the discussed giant clusters with one central $\{(Mo)Mo_5\}$ pentagon which has two adjacent MoO_6 octahedra, only two of the four $\{Mo_8\}$ entities in the $\{Mo_{248}\}$ hub-caps have that structure. The other two $\{Mo_8\}$ units (in green) consist of a central fragment in which six Mo atoms span an $\{Mo_6\}$ octahedron which is linked to two *trans*-positioned edge-sharing MoO_6 octahedra ($\{Mo_8'\}$ entities). The layers of the solid-state structure of Mo_5O_{14} can be formed by formal superposition of the above-mentioned segment with 36 Mo centers $\{Mo_1\}$: yellow, $\{Mo_2\}$: red).

Where are we? Perspectives

Dynamic light scattering experiments on monodisperse solutions containing the $\{Mo_{154}\}$-type cluster show the presence of colloids with a hydrodynamic radius of *ca.* 40 nm which can

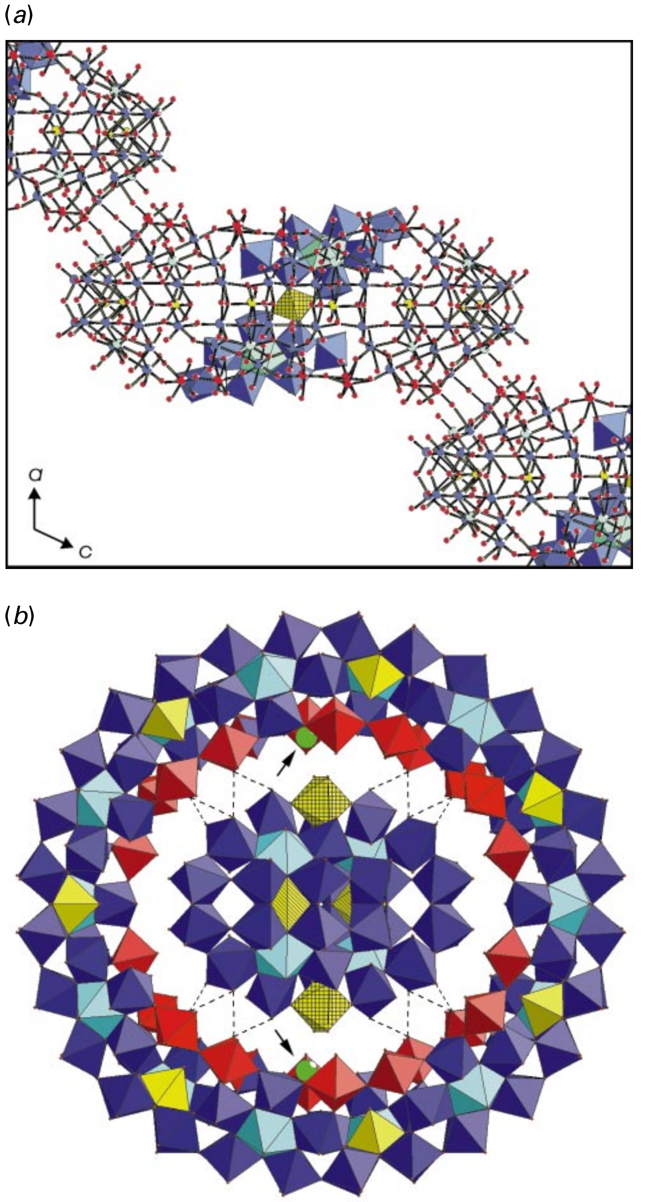


Fig. 20 Some structural details of the novel supramolecular system $\{Mo_{36} \subset Mo_{148}\}$ (occupation of the cavities: *ca.* 20%). (*a*) Part of the chain structure is shown, which is built up by linking ring-shaped cluster units $\{Mo_{148}\}$ (*i.e.* based on the $\{Mo_{154}\}$-type with three missing $\{Mo_2\}$ groups; only the front halves of the rings are shown for clarity). (*b*) View perpendicular to (*a*): the interaction between host and guest is due to 16 hydrogen bonds (dotted lines; O (host) $\cdots$ O (guest) = 2.744–2.965 Å) and (at least) four sodium cations (green, indicated by arrow, only two Na positions are visible in this perspective view) situated between host and guest. The sodium salt crystallizes in the space group $C2/m$ (a = 29.425, b = 51.078, c = 30.665 Å, β = 114.85°).

also be isolated and visualized by scanning electron microscopy (Fig. 21).[29] *As the polyoxometalate chemistry covers therefore several orders of magnitude with respect to the number of atoms and the size of the clusters, its nomination as a "Powers of Ten"-type chemistry in accordance with the famous book title seems justified*. Referring to biological systems we are dealing with an order of magnitude comparable in principle to that of the above-mentioned spherical viruses.

Using combinatorially linkable (virtual) building units (as disposition) in solutions of polyoxometalates having library character, the linking of special groups, such as those of the pentagonal $\{(Mo)Mo_5\}$ type, by different types of linker groups or even paramagnetic (open shell) centers, opens new fascinating aspects and possibilities *e.g.* for structural chemistry, supramolecular chemistry, materials science and magnetochemistry. 'Playing' with pentagons, besides from getting several icosahedral-type clusters, is also of interest because of their role in the history of culture and aspects of solid-state physics.[43] Another interesting option is the study of chemical reactions at the surface of giant clusters, *e.g.* to replace H_2O ligands of the wheel-shaped clusters by amphiphilic (head/tail-type) ligands and place paramagnetic centers at the tail inside the cavity while the head replaces H_2O ligands of the parent system. The most interesting challenge will be of course to fill the cavities of the 'opened' ball-type $\{Mo_{132}\}$ cluster (which exists also as lacunary-type system) or through its apertures with a variety of different guests and also to place molecules inside the cavity of the ring- and ball-shaped clusters, which show a different reactivity to the discrete (isolated) ones.

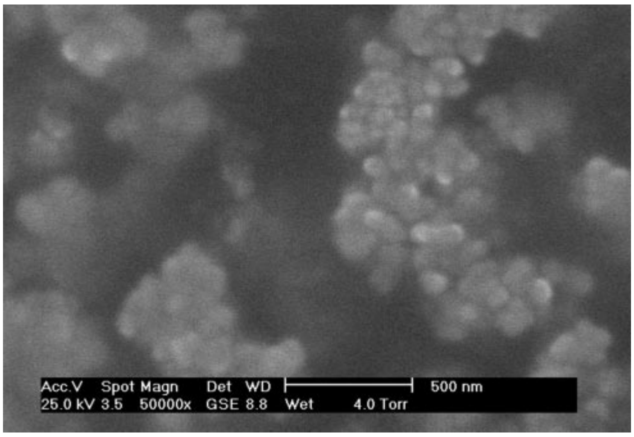


Fig. 21 Scanning electron microscope (Philips ESEM XL30, 25 kV, 3.0 Torr) image showing aggregates with a diameter of *ca.* 500 nm (based on smaller 80 nm particles) which are formed after evaporation of a methanolic solution of $Na_{22}[Mo_{146}O_{442}H_{14}(H_2O)_{58}]\cdot xH_2O$ ($x \approx 250$) (concentration: 0.1 mg ml^{-1}). It is evident that the aggregates tend to form larger arrangements.

Acknowledgements

We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

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Paper 9/01436E