

From simple building blocks to structures with increasing size and complexity[☆]

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Abstract

In Nature, complex molecular systems like proteins have evolved (*natura naturans*) which are perfectly suited to their functions. These are produced in a sequence of steps under dissipative conditions—that is, far from equilibrium. The challenge for the chemist is to

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synthesize correspondingly complex multi-functional molecules also under non-equilibrium (non-dissipative) conditions using multi-component, one-pot reactions, without having to separate and purify each single intermediate product. Relevant model reactions have been discovered in solutions of simple oxoanions of the early transition metals: novel types of molecular growth processes with feedback (including a type of induced cascade) are described leading to different ring-shaped, electron-rich, mixed-valence, giant polyoxomolybdates with nanosized cavities. These can—due to the generation of defects—be covalently linked together to form chains as well as layered mesoporous compounds with properties relevant for materials science. They can also start growing again. The largest polyoxometalate cluster obtained on the basis of this growth process to-date has 248 Mo atoms. Remarkably, such giant ring species can also act as hosts for other clusters forming new types of supramolecular compounds. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Polyoxometalates; Clusters; Supramolecular chemistry

[R.P. Feynman] “I can hardly doubt that when we have some control of the arrangement of things on a small scale we will get an enormously greater range of possible properties that substances can have.” [1]

1. Introduction

Generally, chemists synthesize more complex molecular systems in a step-wise manner through a time-consuming sequential isolation and purification of each intermediate. In the present case of metal–oxide clusters or polyoxometalate chemistry this means for instance that relatively large molecular fragments are functionalized with groups that can be further linked through characteristic reactions: the protonation of highly reactive MoO_3 groups on polyoxometalate clusters results in condensation reactions under H_2O formation (Fig. 1) [2]. Another

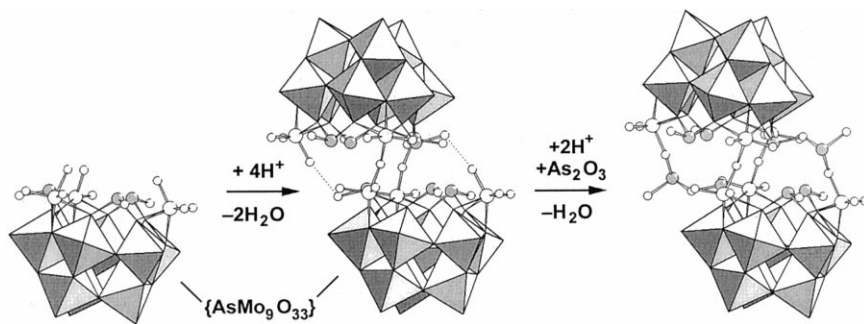


Fig. 1. Based on the functionalization of $\{\text{AsMo}_9\text{O}_{33}\}$ fragments (polyhedral representation) with three highly reactive facial $\{\text{MoO}_3\}$ groups in $[(\text{AsOH})_3(\text{MoO}_3)_3(\text{AsMo}_9\text{O}_{33})]^{7-}$ (left) condensation reactions to $[(\text{AsOH})_6(\text{MoO}_3)_2(\text{O}_2\text{MoOMoO}_2)_2(\text{AsMo}_9\text{O}_{33})_2]^{10-}$ (middle) and $[(\text{AsOH})_4(\text{AsO})_2(\text{HOAsOMoO}_2)_2(\text{O}_2\text{MoOMoO}_2)_2-(\text{AsMo}_9\text{O}_{33})_2]^{8-}$ (right) are possible.

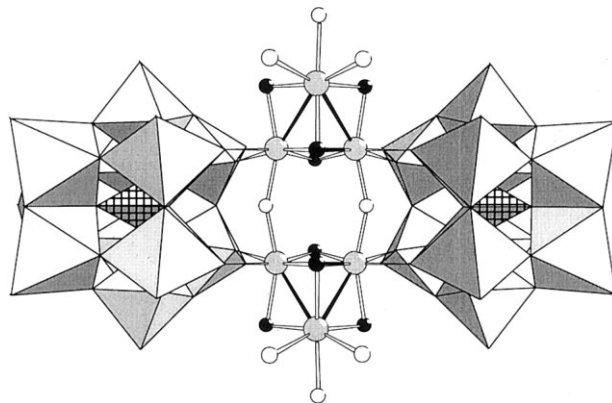


Fig. 2. The cluster $[(\text{SiW}_{11}\text{O}_{39})_2(\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_3)_2(\mu\text{-OH})_2]^{10-}$ is formed by the reaction of two complementary nucleophilic coordinatively unsaturated lacunary Keggin ions $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ with two electrophilic $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ clusters having H_2O ligands as leaving groups.

possibility corresponds to the synthesis of large educts that are complementary to each other, e.g. nucleophilic (N) and electrophilic (E) species, and are subsequently brought to reaction to form the cluster N_nE_m . An example for such a procedure is provided by the coordinatively unsaturated lacunary Keggin structures $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ (N) with electrophilic $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ units (E) to $[(\text{SiW}_{11}\text{O}_{39})_2\{\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_3\}_2(\mu\text{-OH})_2]^{10-}$ whereby water molecules function as leaving groups (see Fig. 2) [3].

In this article we will concentrate on the Feynman approach in pursuing one of the most exciting aims of today's chemistry: the generation of molecular systems with increasing size and functionality or, more specifically, 'en route' from clusters via giant clusters and supramolecular species to materials.

2. Linking building units under self-aggregation conditions

It seems worthwhile to determine initially which general properties building blocks must have in order to allow their reaction to form large multi-functional systems under simple one-pot reaction conditions, thereby avoiding the aforementioned time-consuming and complicated process of several single synthetic steps.

According to our experience, the following conditions favour the corresponding emergence of molecular complexity (in several successive reaction steps) at least in the systems we are investigating:

1. Abundance of linkable units, i.e. building blocks.
2. Possibility of generation of units with high free enthalpy to drive polymerization or growth processes, e.g. by formation of H_2O .

3. Possibility of an easy structural change in the building blocks.
4. Possibility of including hetero elements in the fragments.
5. Possibility to form larger units which can be linked in different ways.
6. Bonding between fragments should neither be too strong nor too weak.
7. Possibility to control the structure-forming processes by templates.
8. Possibility to generate structural defects in reaction intermediates (leading to lacunary structures) by the presence of species which remove building units.
9. Presence of energetically low-lying unoccupied molecular orbitals in the fragments.
10. Possibility to localize and delocalize electrons in different ways in order to gain versatility.
11. Possibility to control and vary the charge (e.g. by protonation, electron transfer reactions, or substitution of building parts).

Under these process conditions it is possible to synthesize step-wise larger molecular systems of a size even comparable to that of proteins. The general principles of relevant one-pot reaction conditions are of interest for problems of prebiotic chemistry, chemical evolution, and conservative self-organization but are, in principle, of industrial interest in the sense of Ugi's multi-component reaction (MCR)-type studies, also [4]. Regarding a prebiotic situation we can cite from an article in *Scientific American* [5] 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 fortuitous formation of a molecule with ability to replicate and evolve—led to life."

In generating large complex molecular systems we have to realize that natural processes are effected by the (directed as well as non-directed) linking of a huge variety of basic and well-defined fragments. An impressive example of this, discussed in virtually all textbooks on biochemistry, is the self-aggregation process of the tobacco mosaic virus, which is based on pre-organized units [6]. This process more or less equates 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 ($\{\text{Mo}_{17}\}$ units) to form cluster anions consisting of two or three of these units provides an archetypical example. The resulting clusters are of the $\{\text{Mo}_{36}\}$ (e.g. $[(\text{MoO}_2)_2(\text{H}_{12}\text{Mo}_{17}(\text{NO})_2\text{O}_{58}(\text{H}_2\text{O})_2)_2]^{12-}$) or of the $\{\text{Mo}_{57}\}$ type (e.g. $[(\text{VO}(\text{H}_2\text{O}))_6(\text{Mo}_2(\text{H}_2\text{O})_2(\text{OH}))_3(\text{Mo}_{17}(\text{NO})_2\text{O}_{58}(\text{H}_2\text{O})_2)_3]^{21-}$) (Fig. 3). Furthermore, the structure of the $\{\text{Mo}_{17}\}$ unit can be reduced to two $\{\text{Mo}_8\}$ -type groups which are linked by $\{\text{Mo}_1\}$ -type units. The $\{\text{Mo}_8\}$ building block is found in many other large polyoxometalate structures [7,8] (see also [9,10]).

3. From the micro- to the mesocosmos

Subsequent to our publication [11] of a wheel-shaped metal–oxide based cluster anion containing 154 molybdenum atoms ($[\text{Mo}_{154}(\text{NO})_{14}\text{O}_{434}(\text{OH})_{28}(\text{H}_2\text{O})_{70}]^{(25 \pm 5)-}$, $\{\text{Mo}_{154}\}$) of 4.1 nm diameter and built up from the aforementioned $\{\text{Mo}_8\}$ groups which are linked by $\{\text{Mo}_2\}$ - and $\{\text{Mo}_1\}$ -type units (Fig. 4), David Bradley metaphorically stated in New Scientist [12]

“Big wheel rolls back the molecular frontier”.

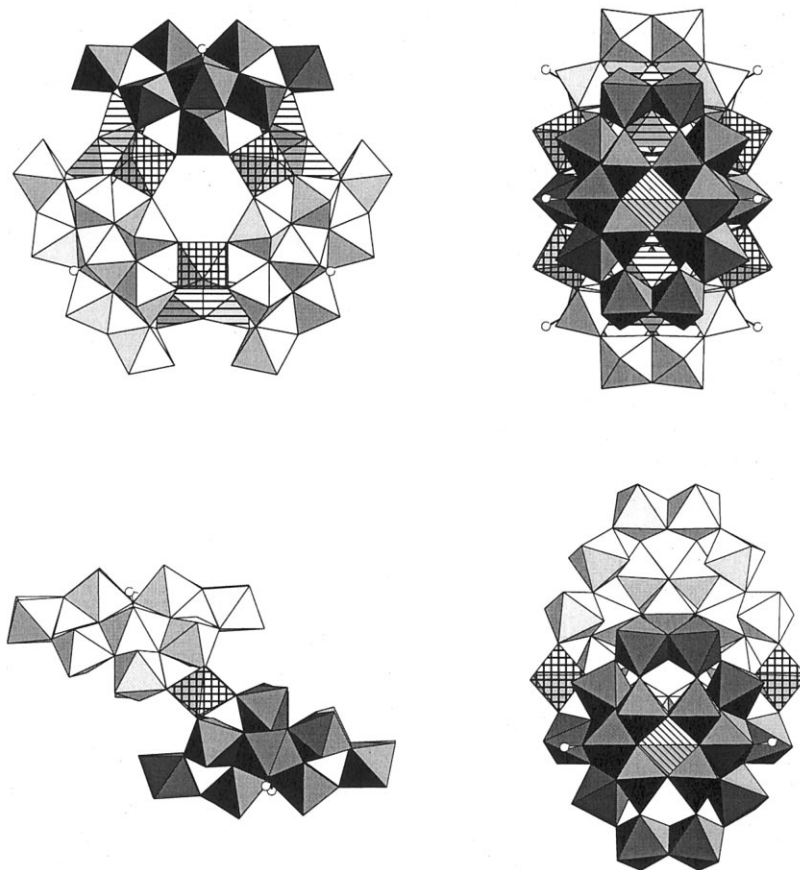


Fig. 3. Polyhedral representation of the cluster $\{\text{Mo}_{57}\}$ with its basic building blocks along the C_3 (upper left) and one of the three C_2 axes (upper right): On the upper right side one $\{\text{Mo}_{17}\}$ group, consisting of two $\{\text{Mo}_8\}$ and one $\{\text{Mo}_1\}$ groups, and on the upper left side three $\{\text{Mo}_8\}$ units. For comparison polyhedral representations of the $\{\text{Mo}_{36}\}$ cluster structure, consisting of two $\{\text{Mo}_{17}\}$ groups linked by two $\{\text{Mo}_1\}'$ units, are shown in the related views, also highlighting one $\{\text{Mo}_8\}$ unit (bottom left) and one $\{\text{Mo}_{17}\}$ unit (bottom right).

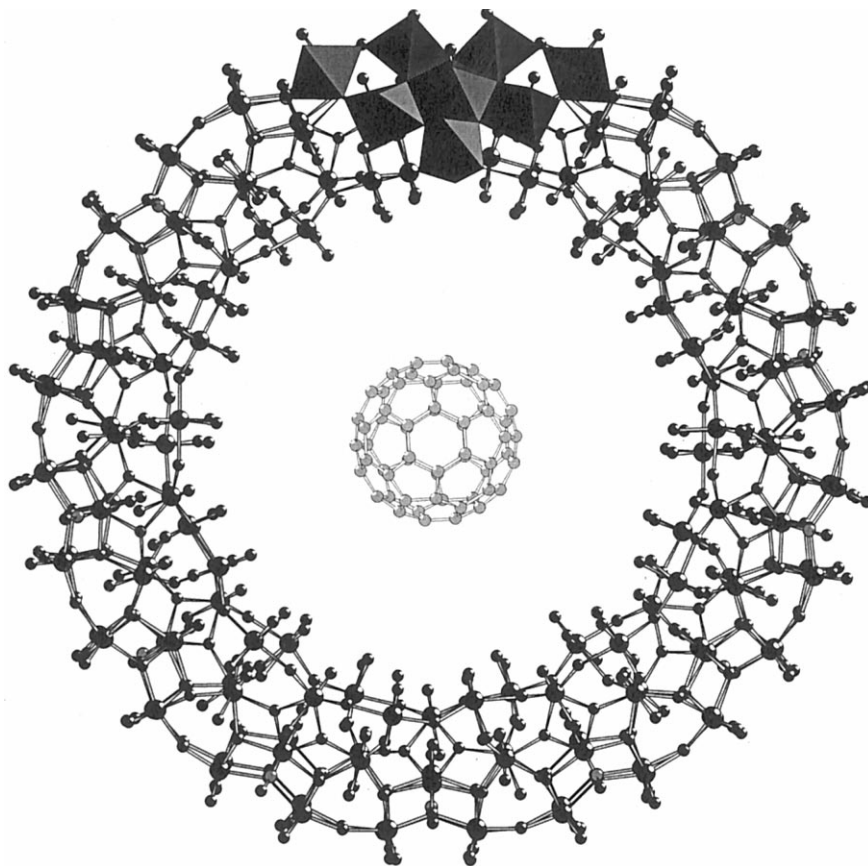


Fig. 4. Ball and stick representation of the cluster anion $\{\text{Mo}_{154}\}$ with one $\{\text{Mo}_8\}$ unit in polyhedral representation. For the purpose of size comparison a C_{60} fullerene molecule is shown.

This signifies the enormous interest of modern chemistry to ‘leave’ the molecular area, characterized by rather small molecules, and to ‘proceed’ to the mesocosmos or nano-world with a view to discovering and investigating the new inherent phenomena and system qualities (see for instance [13]). Suitable systems for such research work are solutions of tetrahedrally shaped oxoanions such as the molybdate anion MoO_4^{2-} : using the same reaction type, i.e. the acidification of the aqueous solution of these oxoanions, the resulting products span three important areas of matter, from the micro-, through the meso- to the macrocosmos, the latter of which is characterized by crystallinity or respectively, translational invariance. In the present case the mesocosmos is of particular interest due to its huge structural variety. Additional external chemical interventions, e.g. those corresponding to Section 2 lead to an even greater structural diversity, in the mentioned case for example by adding reducing agents or templates to the reaction medium.

Remarkably these linkable building units, in the form of Platonic solids, enable the generation of systems of higher structural variability and versatility than is possible with arrangements of metal atoms with spherical symmetry, and lead to pure metal clusters or molecular systems with metal cores. In the first instance, the macroscopic product is the crystalline metal-oxide, in the latter, the crystalline metal (Fig. 5). Important research in this area has been done by Schmid [14] (see also [15]).

4. Template-driven linking results in complementarity between template and reaction product

A first step according to our mentioned concept resembles a template-controlled linking of relatively small building units. It is for instance possible to link square-pyramids built up by five oxygen atoms and a central vanadium atom to form cage systems [16]. The cage, i.e. the cluster shell, is formed complementary to the shape of the template which is finally encapsulated in the reaction product. The relevant condensation process is initiated by adding negatively charged template ions to an aqueous solution containing vanadate ions in the presence of a reducing agent. A spherically shaped halogenide anion (e.g. Cl^-) induces the formation of a spherically shaped cage, whereas the presence of the elongated azide anion results

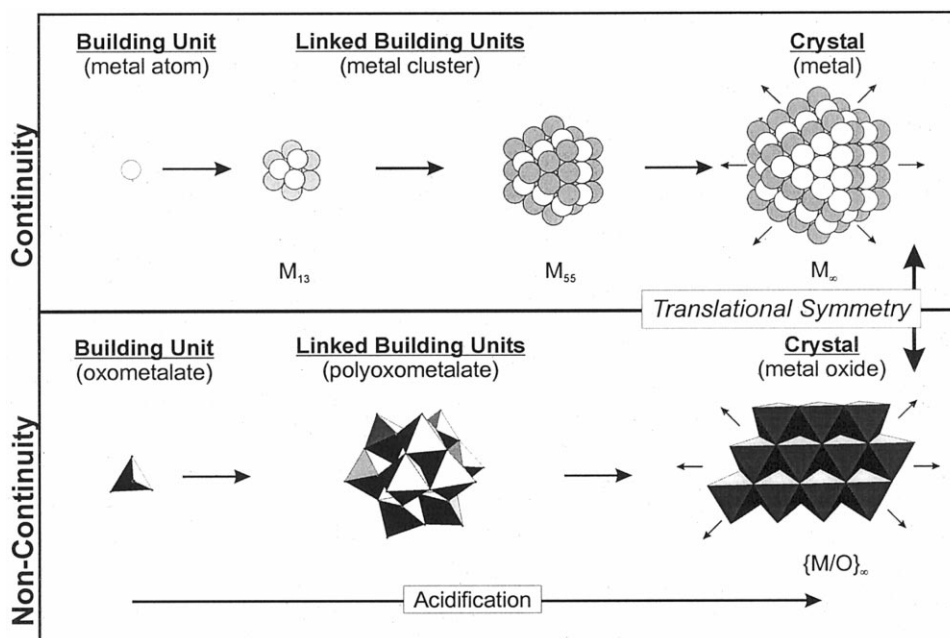


Fig. 5. Schematic comparison of the growth processes leading finally to crystalline metals (upper part) and crystalline metal oxides (lower part respectively).

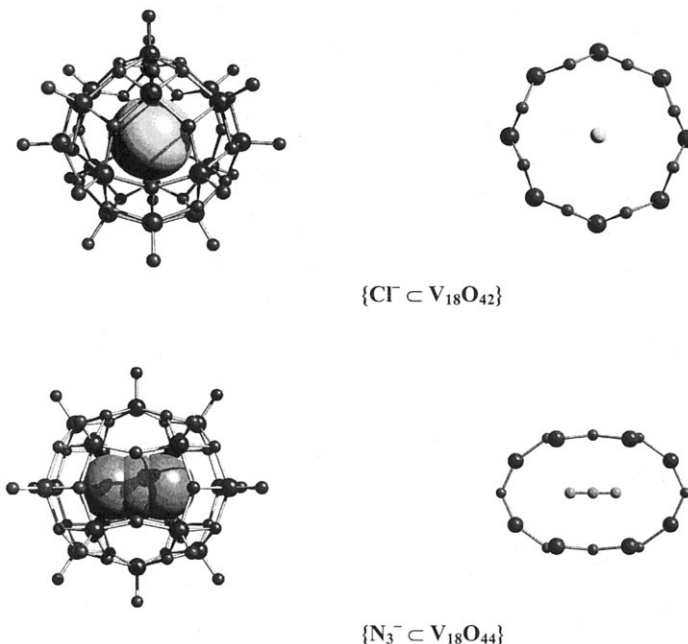


Fig. 6. Complementarity of the polyoxovanadate shell (host) and the encapsulated anion (guest) functioning as template (see text).

in an elongated (stretched) cluster cage (see Fig. 6) [17]. This process can also be formally regarded as slaving according to Haken's concept of synergetics: the template forces or slaves the units to get aggregated in a uniform way. The analogy of this 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 (but in which, on the contrary, metal cations are present) is evident [18]. It is of interest to note that the cluster-shell–anion interaction is very weak [19]. Also remarkable is that all known resulting cluster shells can be regarded as sections of layers of vanadium pentoxide (V_2O_5) ([15]a, [20]). This means that one can describe the cluster cages as being formally cut out from the layers of a lattice of a crystalline compound.

Of particular interest in reference to Section 2 is the case of a template, generated in solution in an initial step, directing or determining the subsequent linking processes: a cubane-type $\{\text{V}_4\text{O}_4(\text{O}_{\text{term}})_4\}$ fragment with the stoichiometry of amphoteric $\text{V}^{\text{IV}}\text{O}_2$, formed primarily in solution, induces the formation of a cluster segment with NaCl defect structure (Fig. 7) [21].

5. Towards larger systems with emergent properties

5.1. Principles

The strategy in the present case is based on the generation of highly negatively

charged fragments (intermediates), which enables growth processes and prevents possible degradation by hydrolysis. This is attained by substitution of metal centers of lower oxidation states for ones of higher oxidation state. Alternatively, the same effect can also be caused by substituting less positively charged for higher positively charged groups (e.g. by exchange of $\{\text{Mo}(\text{NO})\}^{3+}$ for $\{\text{MoO}\}^{4+}$).

If we take the classic Keggin ion $[\text{Mo}_{12}\text{O}_{36}(\text{PO}_4)]^{3-}$, first described by Berzelius (the Nobel laureates Pauling and Werner were attracted by its structure, also), and substitute four V^{IV} for four Mo^{VI} centers a highly charged species results. In the reaction system $\text{MoO}_4^{2-}/\text{H}_2\text{O}/\text{NH}_2\text{OH}$ the corresponding ion with the charge -11 is generated, which for instance can be trapped with an electrophile like As^{III} , resulting in the stable and structurally characterized species $[\text{As}_2^{\text{III}}\text{Mo}_8\text{V}_4^{\text{IV}}\text{O}_{36}(\text{AsVO}_4)]^{5-}$ with a lower negative charge [22]. Other negatively charged fragments form in the solution also, and—in absence of the electrophile As^{III} —they can be linked by certain electrophilic metal centers such as Fe^{3+} or VO^{2+} to form larger systems, leading e.g. to the above-mentioned clusters of the $\{\text{Mo}_{36}\}$ - and $\{\text{Mo}_{57}\}$ -type with two or three negatively charged $\{\text{Mo}_{17}\}$ units [7,8].

5.2. Large clusters and the form/function principle

Increasing the molecular size of the system can in principle lead to multi-functionality—a crucial concept for our work—whereby with increasing size of the system the form/function concept pair correspondingly can become more and more important. In the case of the $\{\text{Mo}_{57}\}$ cluster, it is possible to place or exchange step-wise (para-)magnetic centers like $\text{Fe}^{2+/3+}$ and VO^{2+} in the mentioned linker positions, thus allowing a certain control over the cluster's magnetic properties or even the tuning of these [23]. On the other hand, the cluster in question exhibits non-occupied coordination sites on its periphery. This is of special interest since

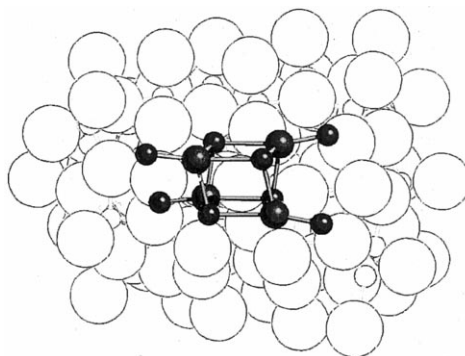


Fig. 7. Structure of the cluster anion $[\text{V}_{34}\text{O}_{82}]^{10-}$ with the highlighted cubane-type central unit $\{\text{V}_4\text{O}_4(\text{O}_{\text{term}})_4\}$ (see text).

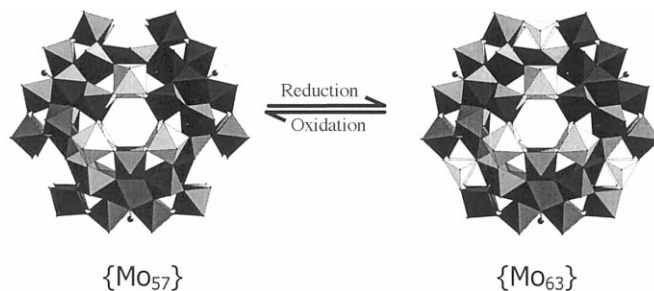


Fig. 8. Quasi-reversible molecular growth within the cluster system $\{Mo_{57}\}/\{Mo_{63}\}$: six $[MoO]^{4+}$ groups can be taken up to form the $\{Mo_{63}\}$ cluster under reducing conditions, and can be expelled when the latter is oxidized (see text).

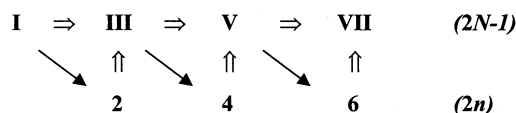
these cavities can be filled with positively charged units like MoO^{4+} under reducing conditions (i.e. by increasing the nucleophilicity) and can be emptied again upon oxidation. Therefore, this reaction represents a type of model for uptake and release of metal centers in metal storage proteins under redox-active conditions as well as model for a molecular switch (Fig. 8) [24].

6. Molecular growth to complexity by symmetry breaks with feedback

Is it possible to generate molecular complexity in a conservative growth process under simple one-pot reaction conditions according to a type of molecular symmetry-breaking steps? Interesting in this context is a type of an induced cascade which is shown in 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 carries information, in the sense of Monod, for the formation of the subsequent intermediate $2n$ which was not originally abundant in solution (induced cascade-type reaction) thus demonstrating an interesting feedback effect.

A first example for a growth process according to this model scheme has been found [24]: a cluster anion containing 37 molybdenum atoms ($[H_{14}Mo_{37}O_{112}]^{14-}$) is



Scheme 1.

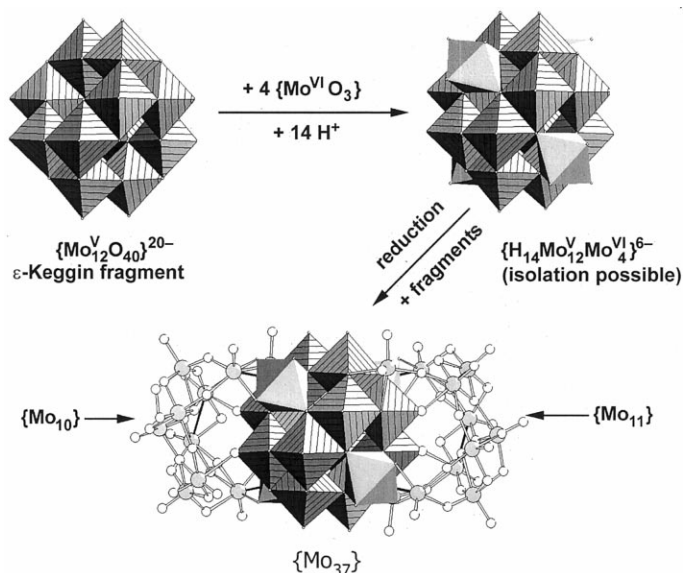


Fig. 9. Molecular growth based on a (molecular) symmetry breaking step according to the reaction Scheme 1 (see text): the resulting cluster $\{Mo_{37}\}$ remarkably does not show any symmetry elements.

formed via pre-intermediates, whereby one of these, the cluster $\{Mo_{12}^V Mo_4^{VI}\}$ (containing an ε -Keggin-type nucleus capped by four $Mo^{VI}O_3$ groups), can also be isolated from the reaction medium [25]. After a reduction process of the type $4 Mo^{VI} \rightarrow 4 Mo^V$ it acts both as nucleophile and template in forming two further electrophilic intermediates ($\{Mo_{10}\}$ and $\{Mo_{11}\}$) which subsequently react with the former template in symmetry-breaking steps leading to the reaction product $\{Mo_{37}\}$ with no symmetry element (Fig. 9).

7. The big wheel: multi-functionality and emergent properties

The stability of the mentioned clusters in solution and the possibility of their spectroscopic detection (e.g. by means of resonance-Raman spectroscopy) are crucial necessities for strategies to synthesize larger species. Stability regions can be determined and further possible aggregation processes under different conditions can be recognized. Starting with the $\{Mo_{36}\}$ -type cluster with two $\{Mo_{17}\}$ groups, the $\{Mo_{57}\}$ -type cluster with three $\{Mo_{17}\}$ groups is formed after adding for instance the electrophilic linker VO^{2+} . In solutions containing this cluster the (reduced more strongly) wheel-shaped cluster $\{Mo_{154}\}$ ($[Mo_{154}(NO)_{14}O_{420}(OH)_{28}(H_2O)_{70}]^{(25 \pm 5)-}$) forms upon further acidification and reduction [11]. This $\{Mo_{154}\}$ cluster (which turned out to comprise the prototype of the molybdenum-blue species [26]) can be regarded as a tetradecamer that meets D_{7d} symmetry if the hydrogen atoms are excluded. It can be formally generated by linking 140 MoO_6

octahedra and 14 $\text{MoO}_4(\text{NO})$ pentagonal square-pyramids. The building blocks of the type $\{\text{Mo}_8\}$, $\{\text{Mo}_2\}$ and $\{\text{Mo}_1\}$ are each present in the cluster 14 times.

The respective publication of this so-called big wheel, which at that time was the largest structurally characterized cluster known, also caused international repercussions in numerous European newspapers, magazines and science magazines—the structure was even painted by an artist who was inspired by its ‘aesthetic beauty’.

The above-mentioned *size/multi-functionality* concept pair can be explained impressively by means of this large cluster:

1. It exhibits a nanometer-sized cavity, presenting new perspectives for a novel host-guest chemistry. In Fig. 4 the cluster’s size is compared to that of a C_{60} molecule.
2. It has an extended hydrophilic inner and outer surface due to the presence of 70 H_2O ligands.
3. The huge surface area in part explains the high affinity towards absorbents, 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 80 nm hydrodynamic diameter could be detected by means of dynamic light scattering.
6. The periphery of the cluster ring shows a rather high electron density.
7. It is possible to generate deliberately discrete structural defects on the inner side of the cluster ring by a formal removal of positively charged $\{\text{Mo}_2\}$ groups.

The aforementioned generation of lacunary-type structures leads to a different reactivity and for instance to the easy linkage of clusters via Mo–O–Mo bonds to form compounds with chains with interesting electronic properties but also compounds with layers. In compounds of the latter type channels are present with basic properties (in contrast to the acidic channels in zeolites), which can ‘take up’ small organic molecules such as formic acid.

From the same above-mentioned building blocks an even larger cluster with 176 molybdenum atoms ($\{\text{Mo}_{176}\}$), i.e. a hexadecameric ring structure, can be derived, containing 16 instead of 14 of each of the three mentioned building blocks correspondingly (Fig. 10) [27]. Even more interesting: under stronger reducing conditions polyoxometalate fragments of the type $\{\text{Mo}_{36}\}$ grow inside the cluster cavity, resulting in a cluster system with 248 molybdenum atoms ($\{\text{Mo}_{248}\}$ cluster). This is in terms of the number of metal atoms the largest known cluster that has been structurally characterized so far [28]. The mentioned ring clusters are formed in the reaction medium in a time scale of a few seconds (observable via resonance Raman spectroscopy), but the exact formation mechanism is unknown until now.

Furthermore, the ring-shaped clusters linked to chains can also act as hosts for smaller polyoxometalate clusters, such as for the $\{\text{Mo}_{36}\}$ -type cluster. In this 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 attraction mediated by four Na^+ cations located in between the negative host and guest (Fig. 11) [28].

In this context important work on large cluster systems based on copper selenide (e.g. $[\text{Cu}_{146}\text{Se}_{73}(\text{PPh}_3)_{30}]$ [29]) and polyoxotungstate systems (e.g. $[\text{As}_{12}\text{Ce}_{16}(\text{H}_2\text{O})_{36}\text{W}_{148}\text{O}_{524}]^{76-}$ [30]) should be mentioned also.

8. Results and outlook

Is the size of such clusters limited or can we fabricate even larger assemblages? Dynamic light scattering experiments on solutions of the $\{\text{Mo}_{154}\}$ -type clusters show the presence of extremely large colloids with a hydrodynamic diameter of ca. 80 nm, the structure of which is as yet unknown [31]. Referring to biological systems we are therefore dealing with a cluster size comparable to that of the mentioned tobacco mosaic virus. Since the discussed polyoxometalate chemistry covers 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. A further challenge lies in the generation of systems with complex macroscopic structures by linking the above-mentioned units in an *open* system (for some theoretical aspects of complex systems see for instance [32])—comparable in nature with the formation of valves of maritime diatoms [33], which are also built up by simple (tetrahedral) element–oxygen building units. Let us close with Hume:

“[...] nothing we imagine is absolutely impossible.” [34]

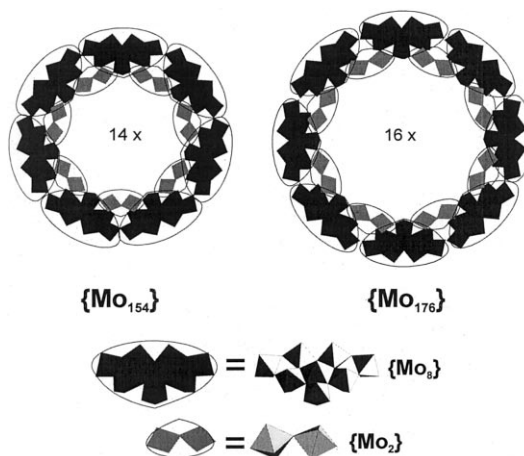


Fig. 10. Schematic comparison of the $\{\text{Mo}_{154}\}$ and $\{\text{Mo}_{176}\}$ cluster types showing the $\{\text{Mo}_8\}$ and $\{\text{Mo}_2\}$ units (the equatorial $\{\text{Mo}_1\}$ units are not visible in this representation).

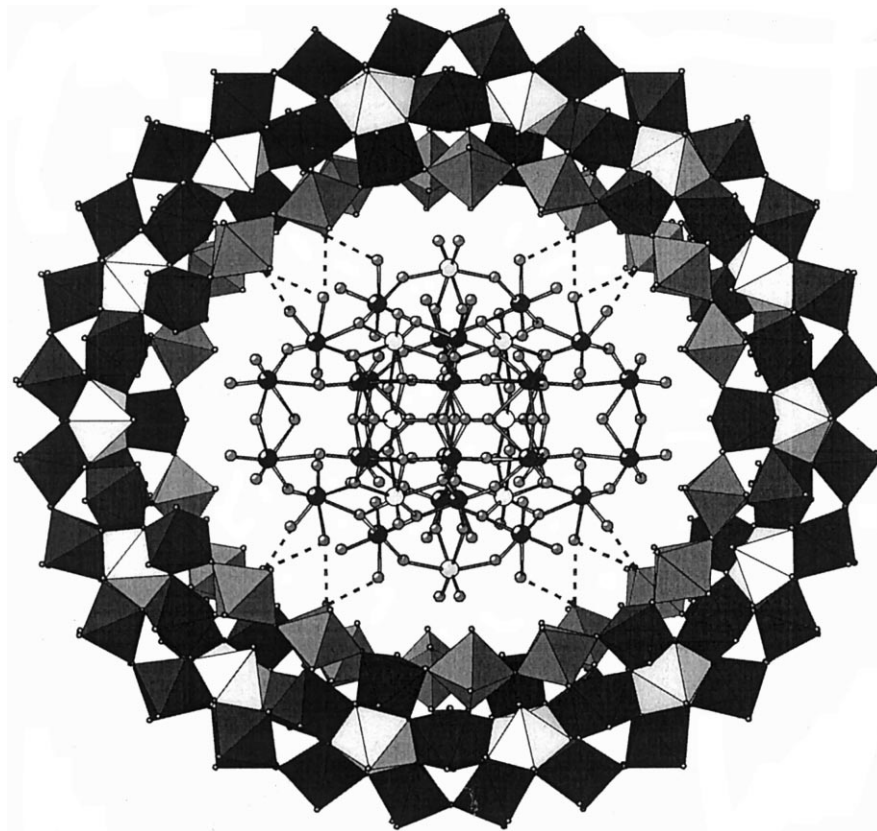


Fig. 11. Some structural details of the novel supramolecular system $\{\text{Mo}_{36} \subset \text{Mo}_{148}\}$ ($\{\text{Mo}_{36}\}$ occupation: 20%). Part of the chain structure is shown, which is built up by linking the ring-shaped clusters $\{\text{Mo}_{148}\}$ with three missing $\{\text{Mo}_2\}$ groups. The interaction between host (in polyhedral representation) and guest (ball and stick) is due to 16 hydrogen bonds (dotted) and four sodium cations situated between host and guest.

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