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En route from the mystery of molybdenum blue via related manipulatable building blocks to aspects of materials science

A. Müller*, S. Roy

Faculty of Chemistry, University of Bielefeld, Postfach 100131, D-*33501 Bielefeld, Germany*

Contents

Abstract

From a unique library containing molybdenum-oxide based building blocks/fragments under reducing conditions in aqueous solution a huge variety of nanoobjects, allowing specific reactions at well-defined positions, can be generated. This enables us to perform a new type of nanochemistry. Examples include: the well-known molecular big-wheel of the type $\{Mo_{154}\}$ and its derivatives and the molecular big-sphere of the type $\{Mo_{132}\}$, the derivatives of which are considered here. In addition the by far largest structurally well characterized cluster with the shape of a lemon is also discussed. After solving the mystery of molybdenum blue, which was the starting point of this type of chemistry, it became evident that the acquired knowledge could be useful for advancing the frontiers of materials science.

Keywords: Materials science; Nano-science; Self-Assembly; Supra-molecular chemistry

> ‘*Where nature finishes producing its own species, man begins, using natural things and with the help of this nature, to create an infinity of species [. . .].*’—Leonardo da Vinci.

1. Introduction

The deliberate synthesis of multifunctional nanosized materials from well-defined building blocks which are abundant in a (virtual) library is one of the most challenging problems in contemporary chemistry. Pertinent targets include the synthesis of materials with especially desirable properties. In solutions of oxoanions of the early transition metals—in particular molybdates under reducing conditions—an enormous variety of compounds can be formed by linking together metal-oxide building blocks [1]. Reasons for this phenomenon are:

1) The easy change of coordination numbers as well as easy exchange of H_2O ligands at Mo sites.
2) The moderate strength of Mo–O–Mo type bonds allowing ‘split and link’ type processes.

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* Corresponding author. Tel.: +49-521-106-6153; fax: +49-521-106-6003.
E-mail address: a.mueller@uni-bielefeld.de (A. Müller).

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3) The easy change and especially increase of electron densities without the strong tendency to form metal–metal bonds.
4) The presence of terminal Mo=O groups preventing in principle unlimited growth to extended structures (see e.g. [2]).

In this review, we will (i) outline the basic chemical principles involved by referring to a model reaction for cluster growth, (ii) describe the building blocks of different molybdenum based cluster anions, (iii) outline relevant major cluster anions together with a brief sketch of the synthetic strategies employed to isolate nanoscaled polyoxomolybdates including those we used to solve the mystery of molybdenum blue solutions [1b] and finally, (iv) refer to interdisciplinary aspects, future perspectives, and possible applications in the field of materials science.

It should be mentioned that for over 200 years, since the time of Scheele and Berzelius, it was not possible to get pure crystalline compounds from the molybdenum blue solutions obtained by reducing an acidified molybdate solution, mainly due to the high solubility of the abundant cluster anions. Destroying the hydration shell of the anions caused by the extremely hydrophilic surface has led to solving this problem [1g,1h]. Following our work and using similar approaches, other research groups world-wide have reported related syntheses in the meantime [3]. Today, it is not only possible to perform a new type of nanochemistry with the clusters but also to dissolve them in organic solvents, e.g. after encapsulating them with suitable surfactant molecules, with the option of forming monolayers, thin films and hybrid materials [4]. Furthermore, it is possible to study their aggregation behaviour leading to the formation of novel vesicles [5]. The most important aspect refers to the fact that the spherical- and wheel-shaped clusters can now easily be obtained with facile syntheses.

2. A model reaction for cluster growth

Molecular growth guards the gateway to molecular complexity. In *nature* complex molecular systems like proteins are formed under conditions far from equilibrium (*natura naturans*). Chemists cherish the dream of attaining complexity correspondingly under one-pot conditions without the problem of repetitive separation and purification of individual products. In practice, an acidified and reduced aqueous molybdate solution provides us with a ‘virtual library’ of building blocks, which is central to an elementary scheme of molecular growth. In this context, we will outline as example a model reaction that was observed in our laboratory [6] (see Fig. 1). In an aqueous molybdate solution α-Keggin type clusters with T_d symmetry can be formed, which upon reduction yield the highly nucleophilic ε-Keggin type clusters $[H_xMo^{V}_{12}O_{40}]^{(20-x)-}$ as intermediates (see Ref. [7] for different aspects of the ε-Keggin ion including the structure of the non-reduced species). These species are stabilized by protonation and by the capture

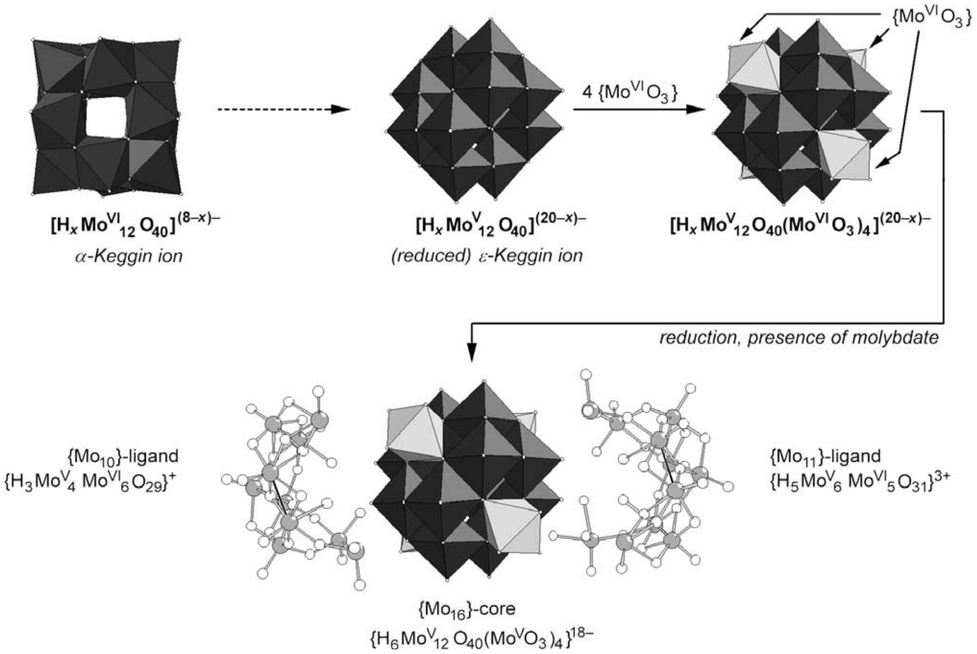


Fig. 1. Demonstration of the stepwise growth process leading to the remarkable cluster anion $[H_{14}Mo_{37}O_{112}]^{14-}$ with no symmetry. The central highly nucleophilic ε-Keggin type $\{H_xMo_{12}O_{40}\}$ core and the four captured $\{MoO_3\}$ groups are shown in black and grey polyhedra, respectively. The $\{Mo_{10}\}$ and $\{Mo_{11}\}$ type ligands are represented as ball-and-stick models (Mo, light grey; O, white).

of four electrophilic $\{Mo^{VI}O_3\}$ groups, thus forming anions of the type $[H_xMo^{V}_{12}O_{40}(Mo^{VI}O_3)_4]^{(20-x)-}$, one of which was isolated with a well-defined protonation and structurally characterized as the $NH_2Me_2^+$ salt [7b,7c]. On further reduction, the originally electrophilic $\{Mo^{VI}O_3\}$ groups become nucleophilic and, in addition, may assume a template function. In a sort of synergistic co-assembly the latter mentioned species further forms and attracts electrophilic polyoxometalate fragments with 10 and 11 molybdenum atoms ($\{Mo_{10}\} \equiv \{H_3Mo^{V}_4Mo^{VI}_6O_{29}\}^+$ and $\{Mo_{11}\} \equiv \{H_5Mo^{V}_6Mo^{VI}_5O_{31}\}^{3+}$). The formation of the related $\{Mo_{37}\}$ type cluster can be regarded as a result of information stored in the intermediate of the type $\{Mo_{16}\}$, i.e. as a result of its template function. The asymmetric growth in this case may be attributed, in principle, to the asymmetric protonation of (only) three of the four μ_3-oxygen atoms forming the central cavity, which may cause an asymmetric charge distribution and protonation on the surface of the intermediate [6]. This reaction where intermediates act as templates for the generation of other intermediates with which the former intermediates react, aptly points to the growth potential of molybdenum based polyoxometalate clusters. A further related case is that of the $\{Mo_{57}M_6\}$ ($M = Fe^{II/III}$, $V^{IV}O^{2+}$) type clusters [6] (see also reviews [1c,1f] and literature cited therein), where six cavities at the surface are capable of undergoing quasi-reversible molecular growth processes, which is controlled by the redox conditions. Under reducing conditions, which increases the nucleophilicity, the cavities can be filled with positively charged electrophilic units like $\{MoO\}^{4+}$ and can be emptied again under oxidizing conditions (Fig. 2). This reaction presents a basic principle of cluster growth: a growing (nucleophilic) species forms and attracts an electrophilic group. Such a model of cluster growth has enabled us to construct clusters of ever increasing complexity, and even the largest inorganic cluster anion with 368 molybdenum atoms is formed correspondingly.

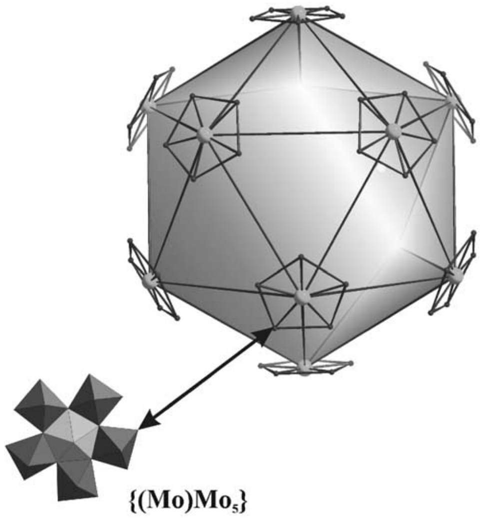


Fig. 3. Construction principle for clusters with icosahedral symmetry. The $\{(Mo)Mo_5\}$ units (polyhedral model with central pentagonal bipyramid in light grey) are the basis for the formation of the $\{(pent)_{12}(link)_{30}\}$ type clusters, where the $\{(Mo)Mo_5\}$ units [1c] define the icosahedron vertices.

3. Playing with pentagons: a structural framework to attain molecular complexity

3.1. The Keplerates

The mentioned $\{Mo_{57}M_6\}$ type clusters as also the largest isopolymolybdate formed under non-reducing conditions [1c,1f] comprise pentagonal $\{(Mo)Mo_5\}$ type building blocks (Fig. 3), each of which consists of a central pentagonal bipyramidal $\{MoO_7\}$ unit sharing edges with five $\{MoO_6\}$ octahedra. Interestingly, the construction of giant spherical systems with icosahedral symmetry requires reaction systems where pentagonal building blocks can be first generated (mainly by a split and link process from a larger fragment), then be linked while getting placed at the 12 corners of an icosahedron. Reaction mixtures of

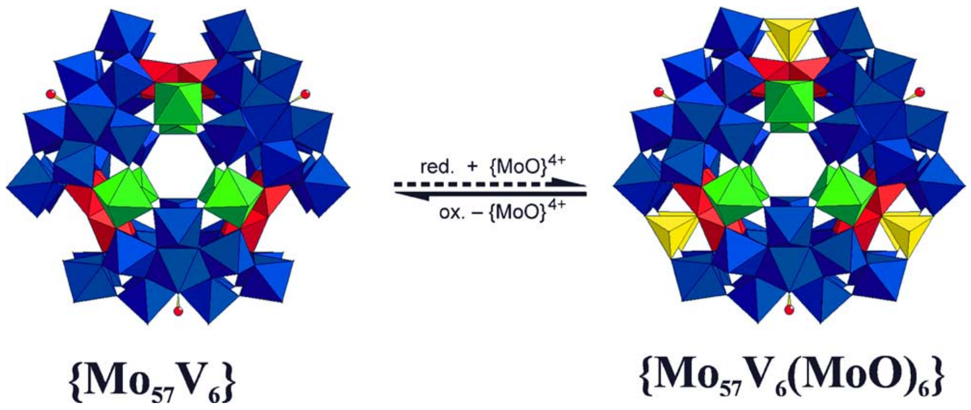


Fig. 2. Uptake and release of $\{MoO\}^{4+}$ groups (formal) in the case of the cluster anions $[H_3Mo_{57}V_6(NO)_6O_{183}(H_2O)_{18}]^{21-}$ and $[H_3Mo_{57}V_6(NO)_6O_{189}(H_2O)_{12}(MoO)_6]^{21-}$, respectively, in polyhedral representation. The central $\{Mo_{57}V_6\}$ core of each anion is built up of three $\{Mo_{17}\}$ units (blue polyhedra) which are linked by three $\{Mo^{V}_2\}$ entities (red polyhedra) and six V^{IV} centres (green polyhedra). The six $\{MoO\}^{4+}$ groups—including the relevant coordinating O atoms of the basic structure—are represented as yellow tetrahedra.

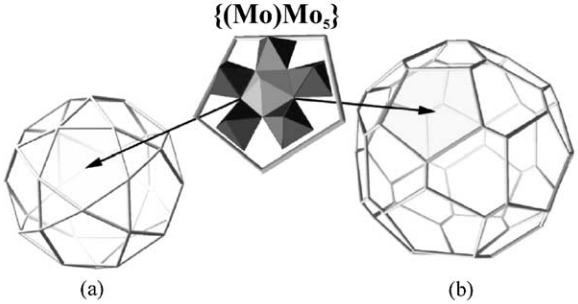
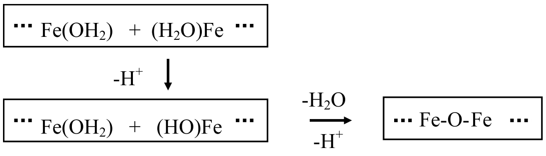


Fig. 4. Structure fragments of spherical giant clusters formed by the mono and binuclear linkers for the pentagons: a (smaller) $\{Fe_{30}\}$ – icosidodecahedron with 12 pentagons and 20 triangles (a) and a (larger distored) $\{Mo_2^v\}_{30}$ – truncated icosahedron with 12 pentagons and 20 hexagons (b).

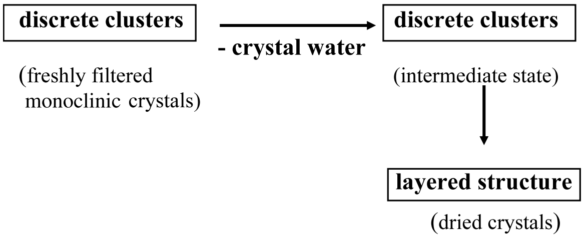
molybdates under appropriate pH values and reducing conditions house a potential library which is ideal for such constructions. In our giant spherical clusters, the pentagonal $\{(Mo)Mo_5\}$ building blocks are placed at the 12 vertices of an icosahedron and linked by a set of 30 mono- or dinuclear spacers, such as $\{Fe(H_2O)\}^{3+}$ [8], $\{Mo^VO(H_2O)\}^{3+}$ [9] or $\{Mo_2^VO_4(CH_3COO)\}^+$ [10]. Of these, the 30 mononuclear linkers for example define an Archimedean solid, the icosidodecahedron with 30 vertices and 32 faces (Fig. 4). Changing the linkers on the one hand provides a means of tuning the size of these nanoscopic objects, and on the other enables us, e.g. in the case of Fe^{III} to construct a giant spherical molecular antiferro-magnet with 150 uncorrelated electrons on its surface! [8]. All such spherical clusters, which can be described by the general formula $[\{(Mo)Mo_5\}_{12}\ \{L\}_{30}]$ or $[(pentagon)_{12}(linker)_{30}]$, belong to the family of ‘Keplerate’ type molecules because of their striking similarity to Kepler’s early model of the universe, as described in his speculative opus *Mysterium Cosmographicum* (see Refs. [1c]11a). A related mathematical study of the family of Keplerates has been published 11b.

3.2. *From self-assembly to self-organization: a room-temperature solid-state reaction with neutral Keplerates*

It is possible—even in a solid-state reaction at room-temperature—to crosslink Keplerates of the type $[\{(Mo^{VI})Mo_5^{VI}\}_{12}\{Fe^{III}\}_{30}]$ comprising Fe centres with H_2O ligands, to form layers [12], following thereby an elementary inorganic condensation reaction with low activation energy. This reaction corresponds to the formation of polycations in a classical reaction at room-temperature (see Scheme 1).



Scheme 1.



Scheme 2.

The rapid loss of water molecules from the freshly filtered crystals, comprising discrete $[\{(Mo^{VI})Mo_5^{VI}\}_{12}\ \{Fe^{III}\}_{30}]$, is the first step in the formation of layered structures (see Scheme 2 and Fig. 5). The easy loss of water and the easy crosslinking is due to the fact that the clusters are neutral. The reaction steps (see Schemes 1 and 2) show the decrease in the volume of the unit cell corresponding to the decrease in the number of crystal water molecules.

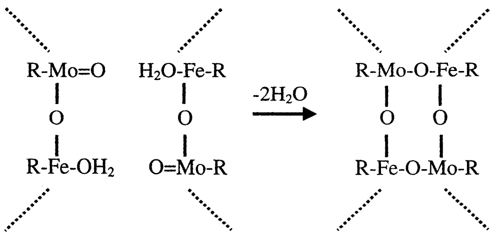
Another reaction of this type is also known and is based on a compound containing practically neutral $[\{(Mo^{VI})Mo_5^{VI}\}_{12}\{Mo_6^VFe_{24}^{III}\}]$ clusters. When the crystals containing the discrete clusters are dried the clusters become linked to form 1D chains initiated by the rapid loss of crystal water molecules (Figs. 6 and 7) [13]. The initial loss of these molecules causes a decrease of inter-sphere distances, which leads to the situation that an Mo=O group of one sphere formally acts as a ligand while replacing H_2O groups of an adjacent sphere in an S_N-type reaction as shown in Scheme 3.

These types of reactions are essentially entropy driven.

The Keplerate cluster formation is an example of self-assembly built up according to an *‘aufbau’ principle*. On the other hand, the subsequent formation of a paramagnetic necklace, i.e. a chain of Keplerates or the larger structure mentioned above, presents a perfect example of self-organization where the discrete units ‘act’ self-determinedly (for related aspects see for instance [14]).

3.3. *Host–guest chemistry with Keplerates*

Can Keplerates play ‘*hosts*’? The presence of large spherical cavities makes them attractive candidates. A model inves-



Scheme 3.

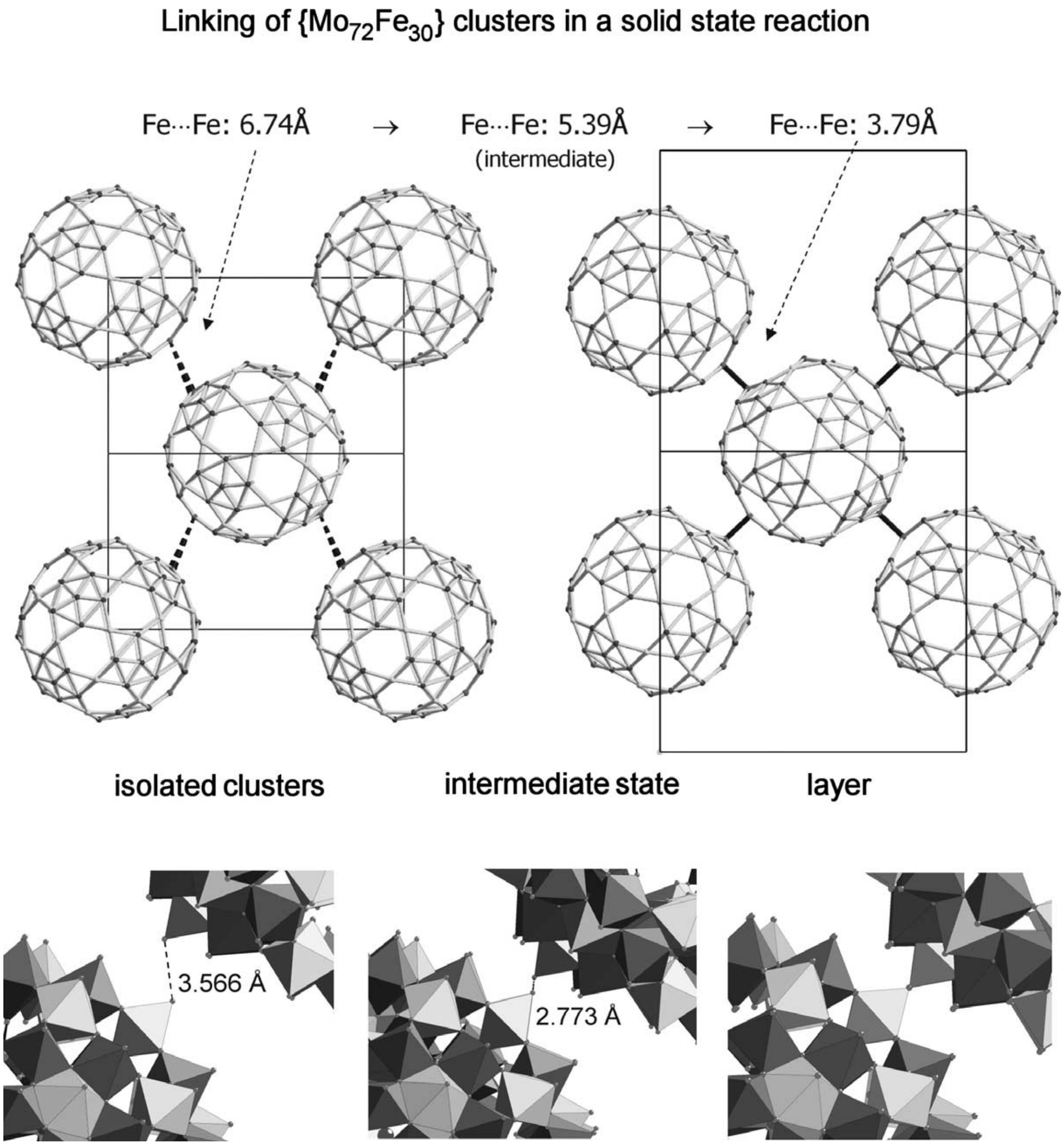


Fig. 5. Wireframe representation of the metal skeleton of the $\{Mo_{72}Fe_{30}\}$ type cluster units indicating their covalent crosslinking to a layer structure (top right). The solid-state room-temperature conversion process leading to its formation takes place according to Scheme 1 and Scheme 2 given in the text. The reaction proceeds from discrete cluster units (top left) present in the wet monoclinic crystals—freshly filtered from the mother liquor—via an intermediate state with discrete units positioned at the minimum possible distance without bond formation to the final (rhombic) crystalline product (not valid for rhomboliedral crystals with discrete units [8]).

tigation revealed that the $[\{(Mo^{VI})Mo_5^{VI}\}_{12}\{Fe^{III}\}_{30}]$ Keplerate can serve to host Keggin ions (diameter ca. 14 Å) in its cavity, a fact first realized by our former co-worker Samar Das. We succeeded in incorporating the latter into the cavity of the former just by adding the Keggin ion to a solution ambient to the generation of the cluster shells [15]. The resulting molybdenum-oxide based composite with encapsulated Keggin ion presents an unprecedented non-covalent, i.e. supramolecular host–guest interaction (Fig. 8). (Here the Keggin ion (guest) can, in principle, also act as a template for the generation of the Keplerate (host).) The interactions between the constituents are strictly non-covalent, i.e. hydrogen bonding, in nature. An even more interesting aspect is that the crosslinking of these supramolecular nanocomposites is identical to the linking of the empty capsules to form layers.

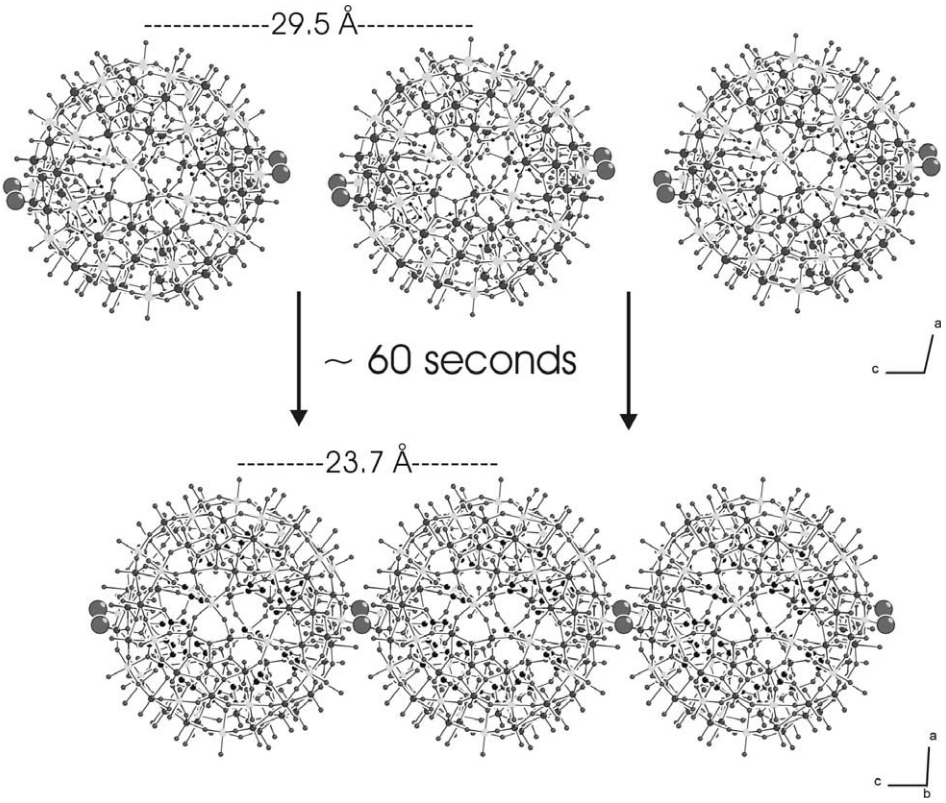


Fig. 6. Schematic demonstration of the room-temperature solid-state reaction (see also Fig. 7) leading to the formation of the chain (bottom) present in $Na_2[\{(Mo^{VI})Mo_5^{VI}\}_{12}\{Mo_6^{V}Fe_{24}^{III}\}(CH_3COO)_{20}O_{258}(H_2O)_{82}]\cdot$ca. $80H_2O$ caused by linking the discrete spheres $[\{(Mo^{VI})Mo_5^{VI}\}_{12}\{Mo_6^{V}Fe_{24}^{III}\}(CH_3COO)_{20}O_{258}(H_2O)_{84}]^{2-}$. Note the small error limit in the number of Mo^{V} centres and the corresponding possible cluster charge.

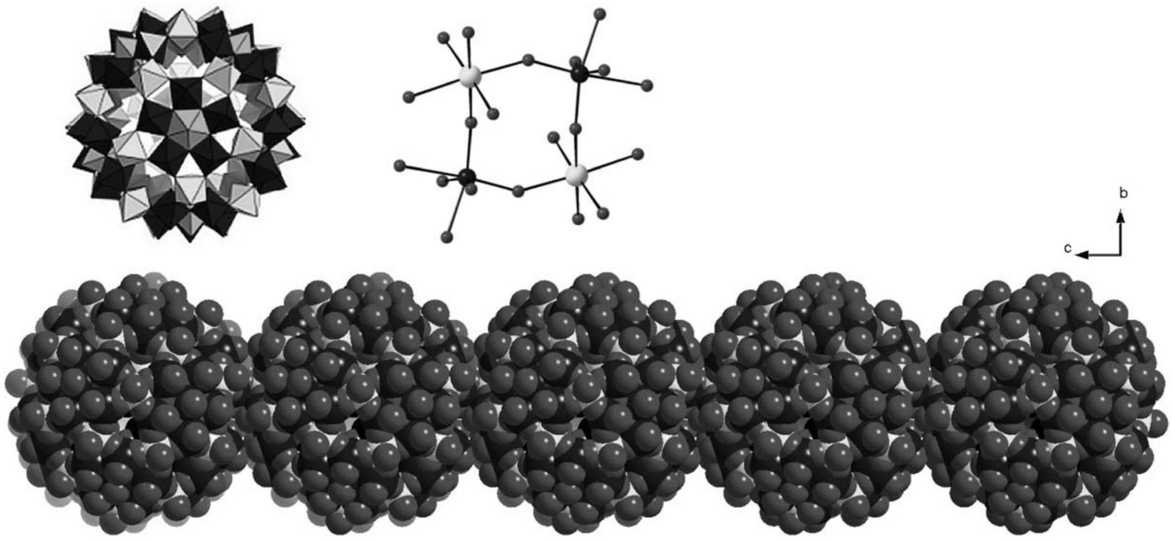


Fig. 7. More detailed representation of the structures depicted in Fig. 6 showing the discrete anion $[\{(Mo^{VI})Mo_5^{VI}\}_{12}\{Mo_6^{V}Fe_{24}^{III}\}(CH_3COO)_{20}O_{258}(H_2O)_{84}]^{2-}$ (polyhedral representation) in crystals of $Na_2[\{(Mo^{VI})Mo_5^{VI}\}_{12}\{Mo_6^{V}Fe_{24}^{III}\}(CH_3COO)_{20}O_{258}(H_2O)_{84}]\cdot$ca. $150H_2O$, and of the chain in crystals of $Na_2[\{(Mo^{VI})Mo_5^{VI}\}_{12}\{Mo_6^{V}Fe_{24}^{III}\}(CH_3COO)_{20}O_{258}(H_2O)_{82}]\cdot$ca. $80H_2O$ (space-filling representation). The linking area is separately given in ball-and-stick representation (top right); bond lengths [Å] and angles [°] in the M_4O_4 (M = Mo/Fe) ring: Mo–O: 1.72/1.78; Fe–O: 1.96/1.98; Mo–O–Fe: 147.0/149.9; O–Mo–O: 101.5; O–Fe–O: 93.2) [13].

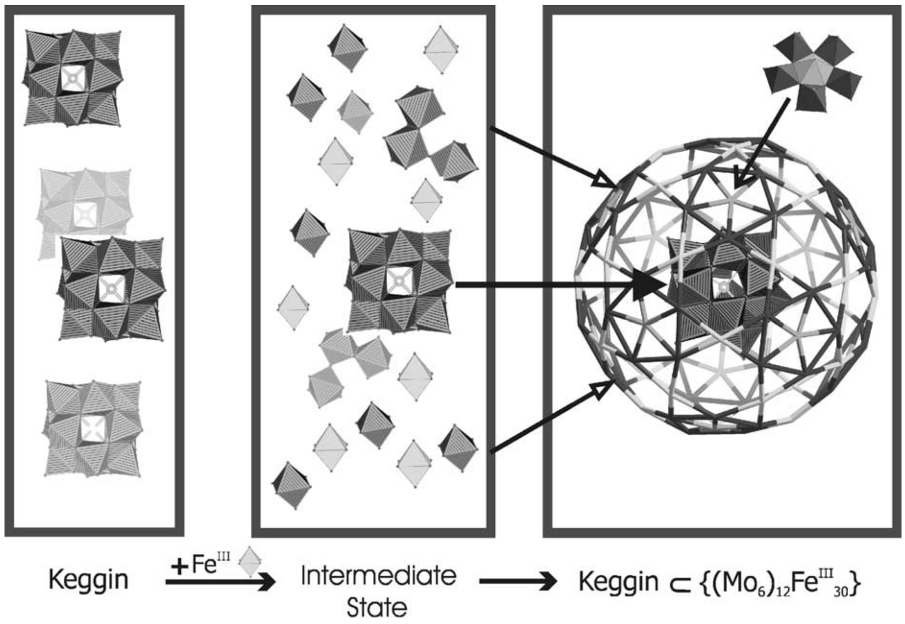


Fig. 8. Reaction scheme showing the decomposition of part of the Keggin anions $\{PMo_{12}O_{40}\}^{3-}$ (left, polyhedral representation) in the presence of Fe^{3+} and leading finally to the formation of the $\{(Mo)Mo_5\}_{12}\{Fe\}_{30}$ type cage (with wireframe representation of the capsule's Mo atoms in dark grey and Fe atoms in light grey) which has the remaining non-decomposed Keggin anions encapsulated (polyhedral representation) thus forming the unusual supramolecular species with coreshell topology: guest $\subset \{(pent)_{12}(link)_{30}\}$ (FeO_6 octahedra light grey).

4. Returning to pentagons: 'big-wheels' and allied clusters

4.1. *From Keplerates to molecular big-wheels: pentagons lead the way*

The mentioned Keplerates are results of the 'spherical disposition' of pentagonal $\{(Mo)Mo_5\}$ building blocks with a C_5 symmetry whereas a 'circular disposition' of the deformed $\{(Mo)Mo_5\}$ unit leads to the formation of $\{Mo_{154}\}$ and $\{Mo_{176}\}$ type clusters, commonly known as the *big-wheel* or *giant-wheel* type species, respectively. Their structures can formally be represented as $[\{(Mo)Mo_5\}\{Mo_2\}\ \{Mo_1\}]_m$, where $m = 14$, 16 for $\{Mo_{154}\}$ (Fig. 9) and $\{Mo_{176}\}$, respectively. The $\{Mo_{154}\}$ cluster has an external diameter of 3.4 nm while that of $\{Mo_{176}\}$ is 4.1 nm [16,17]. It is now also possible to obtain the $\{Mo_{176}\}$ type cluster starting from the $\{Mo_{132}\}$ type Keplerate via a mild oxidation reaction catalyzed by metal cations (this represents the best available method) [16], while the $\{Mo_{154}\}$ cluster can now be obtained by a very facile method [1b,1g,1h,13].

4.2. *Derivatives of the 'wheels': The route to complexity*

In addition to the pentagonal $\{(Mo)Mo_5\}$ unit, the wheel type polyoxomolybdates contain as mentioned above $\{Mo_2\}(\equiv\{Mo_2O_5(H_2O)_2\}^{2+})$ together with $\{Mo_1\}$ type units. Employing simple chemical techniques (for instance raising the pH, or prolonging crystallization time) we succeeded in designing new clusters with defects, i.e. with n missing $\{Mo_2\}$ units (where $n = 5$, 6) [18,19]. It has even been possible to incorporate other metal ions like Cu^{2+} into the 14 or 16 tetrahedral cavities marked by four O atoms, normally occupied by protons in the parent cluster [20] (Fig. 10). In this context, it is worth mentioning that all wheel type clusters like $\{Mo_{154}\}$ or $\{Mo_{176}\}$ contain electronically uncoupled 14 or 16 incomplete double cubane type $\{Mo_5O_6\}$ compart-

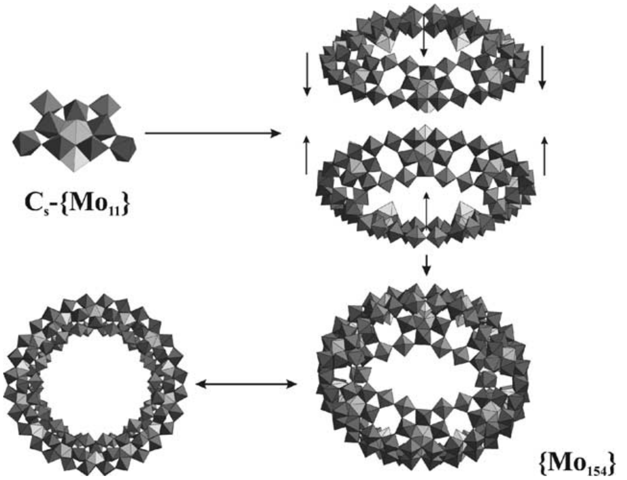


Fig. 9. A formal building scheme for an $\{Mo_{154}\}$ ring starts from a C_s type $\{Mo_{11}\}$ unit (top left), fourteen of which are fused together to form two $\{Mo_{77}\}$ belts (top right). Two of these are fused together after one belt has been rotated by an angle of 360°/14 with respect to the other along the C_7-axis to form the wheel type species.

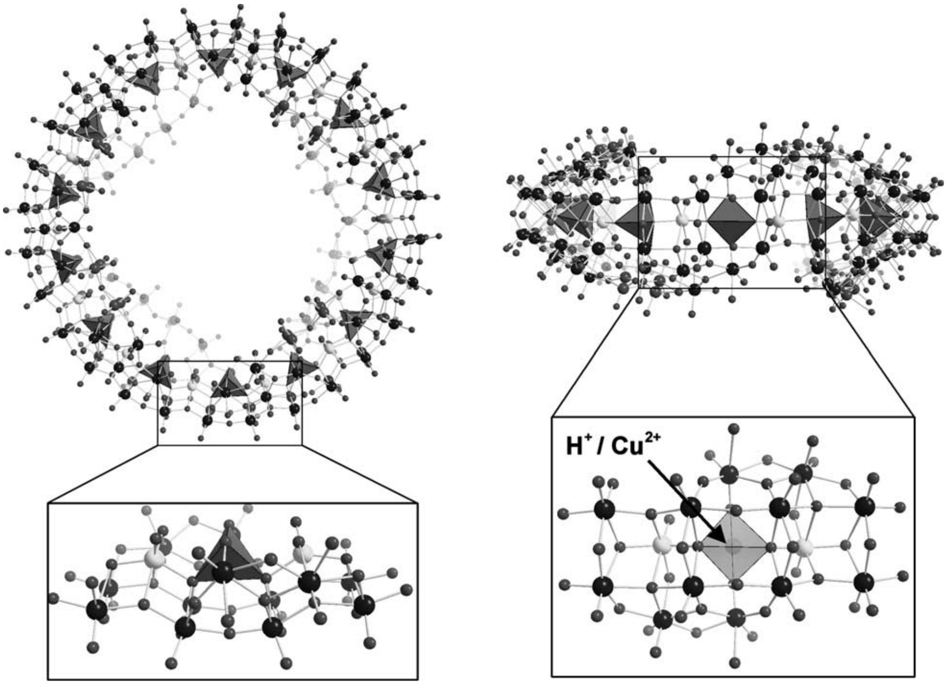


Fig. 10. Molecular structure of the cluster anion $[\{\mathrm{Mo}_8^{\mathrm{V/VI}}\mathrm{O}_{26}(\mu_3\mathrm{O})_2\mathrm{X}_i(\mathrm{H_2O})_3\mathrm{Mo}^{\mathrm{V/VI}}\}_{14}\{\mathrm{Mo}_2^{\mathrm{VI}}\mathrm{O}_5(\mathrm{H_2O})_2\}_8]^{26-}$ ($\sum X_i = 4\mathrm{H} + 5\mathrm{Cu}$) in ball-and-stick representation (top and side view) while the O_4 tetrahedra (grey) which encapsulate Cu^{2+} centers (disordered) are given in polyhedral representation (left); additionally, one relevant segment is highlighted separately (right).

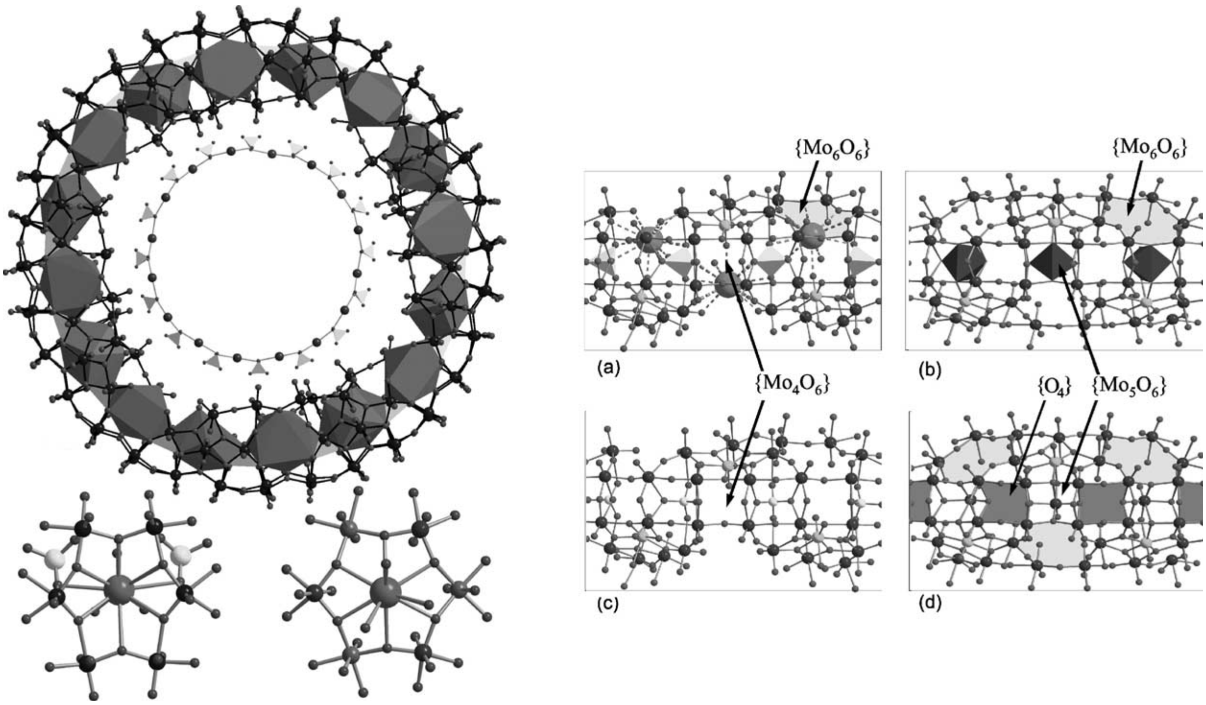


Fig. 11. Left: structure of $[\mathrm{Mo}_{114}^{\mathrm{VI}}\mathrm{Mo}_{32}^{\mathrm{V}}\mathrm{O}_{429}(\mathrm{H_2O})_{50}(\mathrm{KSO_4})_{16}]^{30-}$ (top and partial side view) in crystals of $\mathrm{K}_{14}\mathrm{Na}_{16}[\mathrm{Mo}_{114}^{\mathrm{VI}}\mathrm{Mo}_{32}^{\mathrm{V}}\mathrm{O}_{429}(\mathrm{H_2O})_{50}(\mathrm{KSO_4})_{16}]\cdot$ca. $500\mathrm{H_2O}$ in ball-and-stick representation showing the KO_{11} units (in polyhedral representation) to demonstrate the overall K environment (see Ref. [21] for further details including the receptor description at the bottom.). Right: Demonstration of the multitude of specific adjacent receptors (forming a zigzag ring) (d) for 16 K^+ (nucleophilic $\{\mathrm{Mo_6O_6}\}$ rings light grey, indicated by arrows in (a) and (b)) and 16 SO_4^{2-} ions (sites between $\{\mathrm{Mo_5O_6}\}$ compartments in dark grey and marked in (d) by $\{\mathrm{O_4}\}$). The change from the ‘classical’ $\{\mathrm{Mo_2Mo_8Mo_1}\}_\mathrm{n}$ type (b, d) [1c] to the $\{\mathrm{Mo_2}\}_{n-x}\{\mathrm{Mo_8}\}_\mathrm{n}$ type (a, c) ring structure involving the change of the $\{\mathrm{Mo_5O_6}\}$ [1c] to the $\{\mathrm{Mo_4O_6}\}$ unit by release of $\{\mathrm{Mo_1}\}$ is demonstrated, too (released $\{\mathrm{Mo_1}\}$ units dark grey octahedra in (b), SO_4^{2-} light grey tetrahedra, K^+ emphasized in (a) as grey spheres).

ments with two delocalized Mo (4d) electrons [1b]. The Cu^{2+}-containing cluster anion is a derivative of the aforementioned tetradecameric $[\{Mo_8\}\{Mo_2\}\{Mo_1\}]_{14}$ type cluster with six missing $\{Mo_2\}$ units, bearing the formula $[\{Mo_8^{V/VI}O_{26}(\mu_3O)_2X_i(H_2O)_3Mo^{V/VI}\}_{14}\{Mo_2^{VI}O_5(H_2O)_2\}_8]^{26-}$ $(\sum X_i = 4H + 5Cu)$. An interesting aspect is the change in the electronic structure of this cluster compared to the parent $\{Mo_{154}\}$ cluster. In the former, the electronic spectra show an absorption band at ca. 520 nm due to the abundance of Cu^{2+} ions in addition to the usual band observed due to an IVCT $(Mo^{V} \rightarrow Mo^{VI})$ type electronic transition, for which a blue shift is observed due to the influence of Cu^{2+} on the delocalized Mo (4d) electrons in the $\{Mo_5O_6\}$ compartments [20].

Incorporation of potassium and sulfate ions in the parent $\{Mo_{176}\}$ type cluster at well-defined receptors presents an interesting perspective for a type of super-supramolecular chemistry [21]. In the related reaction all 16 $\{Mo_1\}$ units are expelled from the cluster, with the result that instead of the 16 aforementioned classical $\{Mo_5O_6\}$ compartments a new type of $\{Mo_4O_6\}$ compartment is generated (see Fig. 11). The release of 16 $\{Mo_1\}$ units provides room for encapsulation of 16 K^+ ions beneath the nucleophilic $\{Mo_6O_6\}$ crown ether type rings present on the surface of the cluster (for a comparable situation of spherical clusters with the same rings see [22]). The 16 $\{O_4\}$ type 'cavities' between the $\{Mo_4O_6\}$ compartments here encapsulate *formally* S^{6+} instead of Cu^{2+} as observed in the previous example or H^+ in the parent cluster. (This situation can be compared with the O_4 cavity of the Keggin ions.) Considering the potassium and sulfate ions alone, this cluster shows an unusual 64-membered $\{KOSO\}_{16}$ type ring where the 'bidentate' SO_4^{2-} shows relevant $K \cdots O$ distances of the order of 3.0 Å (see Fig. 11). Some other derived structures with lanthanide ions like Pr^{3+}, Eu^{2+} are also known, in which the incorporated lanthanide ions influence the overall cluster's curvature with the option of their sizing or the generation of completely new and complex structures (for details see Refs. [23,24] and Fig. 12).

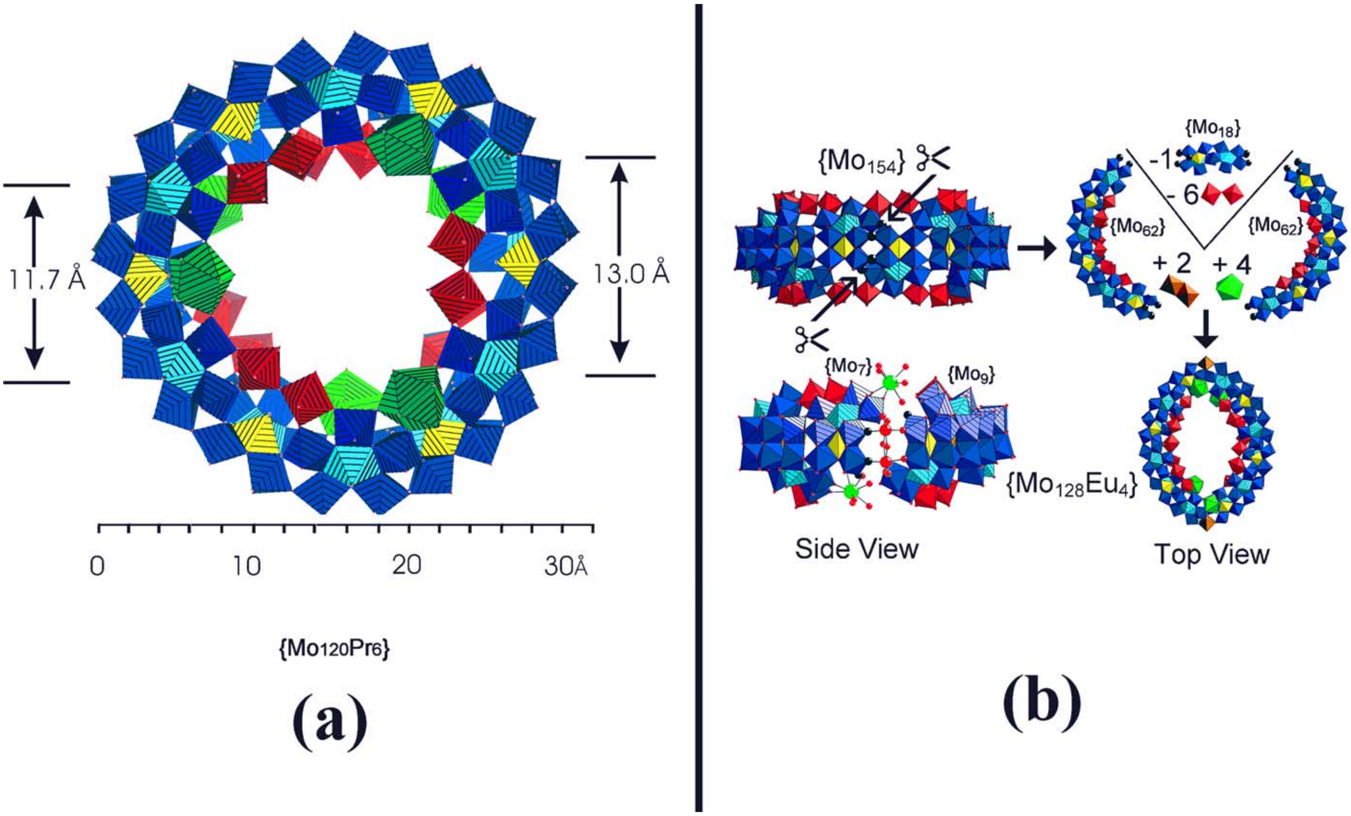


Fig. 12. (a) Structure of the symmetrical ring shaped anion $[Mo_{120}O_{366}(H_2O)_{48}H_{12}\{Pr(H_2O)_5\}_6]^{6-}$ in polyhedral representation with $\{Mo_1\}$ units in yellow, $\{Mo_2\}$ in red, $\{Mo_8\}$ units (including the central pentagonal bipyramids) in blue, and the $(\{PrO_4(OH_2)_5\}$ polyhedra in green (constituents of the lower half of the ring are more pale in color). The two marked distances between two equivalent pentagonal bipyramids are a measure of the curvature, which is greater if a $\{Mo_2\}$ unit is replaced by a Pr^{3+} cation. (b) Demonstration of how a non-symmetrical $[\{Mo_{128}^{VI/V}Eu_4O_{388}H_{10}(H_2O)_{81}\}_2]^{20-}$ ring can formally be constructed from the parent $\{Mo_{154}\}$ type cluster according to a 'cutting' process based on a molecular scissors giving the two shown large basic $\{Mo_{62}\}$ fragments. Top left: side view of the parent $\{Mo_{154}\}$ ring, (cutting positions marked). Top right: those units which have to be removed from the $\{Mo_{154}\}$ ring and those which have to be added to the resulting two large fragments to generate the giant cluster. Bottom: the complete cluster from a side and top view (color code as in (a); new $\{Mo^{*2}\}$ units in borwn; EuO_9 polyhedra and Eu atoms (left) in green; MoO_6 octahedra of a selected $\{Mo_7\}$ and a $\{Mo_9\}$ group, respectively, as hatched violet polyhedra).

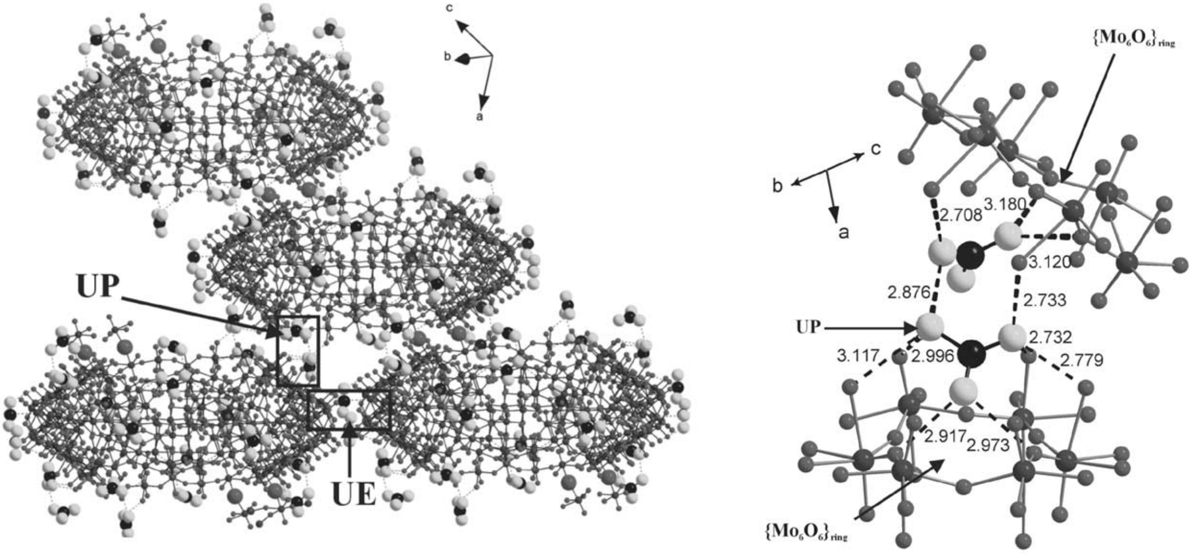


Fig. 13. Left: ball-and-stick representation of four $\{Mo_{154}\}$ type rings of the compound ${}^{1}_{\infty}\{(NH_3CONH_2)_{14}[Mo^{VI}_{126}Mo^{V}_{28}O_{462}H_{14}(H_2O)_{68}]\}\cdot$ca. $350H_2O$ 'glued' with two types of protonated urea molecules [viz., equatorial (UE) as well as polar (UP)]. The atoms of the urea (type) units and the oxygen atoms which covalently connect adjacent rings have been enlarged for clarity (carbon black; nitrogen and oxygen atoms of urea units which could not clearly be distinguished using single-crystal X-ray structure analysis, light grey). Right: interaction between polar UP type units among themselves as well as with oxygen atoms of two hexagonal $\{Mo_6O_6\}$ ring sites with the potential receptor property of the cluster. The difficulty to distinguish exactly between O and N atoms of UP is mainly caused by a $O{=}Mo{-}H_2O$ disorder at the cluster surface (see also related distances in Å).

4.3. Connecting the 'wheels' to chains: designing novel hosts

Like Keplerates, the $\{Mo_{154}\}$ type wheels can also be 1D linked to form a chain for instance by the use of urea as gluing agent; urea reduces the repulsion of approaching negatively charged rings, thereby facilitating condensation between them and ultimately leading to covalent Mo–O–Mo connectivity (see Fig. 13 and Ref. [25]). This can lead us to new gateways in host–guest chemistry as the protonated urea cations are 'attached' to the nucleophilic $\{Mo_6O_6\}$ type receptors on the cluster surface. It has also been possible to put 'sterically befitting' $\{Mo_{36}\}$ clusters into the cavity of related ring type $\{Mo_{148}\}$ clusters linked to a chain to form a novel supramolecular host–guest system. Here the interaction between the host 'holds' the guest mainly by 16 hydrogen bonds between them (Fig. 14).

5. Inorganic chemistry goes protein-size: $\{Mo_{368}\}$, the 'Blue Lemon'

> '*It may look like a lemon, but a hollow nanocluster made from molybdenum-oxide shows just how sophisticated inorganic nanostructures can be.*'—P. Ball [26].

Indeed, molybdenum-oxide based fragments display under reducing conditions an extreme flexibility which fulfills the most important prerequisite for forming an overwhelming variety of sophisticated nanostructured landscape functionalities. The special building units abundant in a potential 'dynamic library' can form, via a type of 'split and/or link process' (for instance the generation of the mentioned $\{(Mo)Mo_5\}$ units from larger ones which subsequently get linked) a class of molecular architectures upon slight variation of the boundary conditions. The $\{Mo_{368}\}$ cluster [2] is such a molecular type (Fig. 15). Comparable to the size of hemoglobin (external diameter ca. 6 nm), this species is formed by the linking of 64 $\{Mo_1\}$, 32 $\{Mo_2\}$, and 40 $\{(Mo)Mo_5\}$ type units (32 with sulfate ligands and 8 without; this was erroneously mentioned in Ref. [2]) via a remarkable symmetry breaking process nicely noticeable on its surface. The structure of the cluster anion can be considered as a hybrid between the $\{Mo_{176}\}/\{Mo_{154}\}$ type giant molecular wheels and the $\{Mo_{102}\}/\{Mo_{132}\}$ type clusters. The hybrid character manifests itself in the occurrence of 24 C_5 type $\{Mo_{11}\}$ units of the $\{Mo_{132}\}$ type spherical shaped clusters together with 16 C_s type $\{Mo_{10}\}$ fragments of the related wheel shaped clusters having only one $\{MoO_6\}$ octahedron less. Although the C_5 $\{Mo_{11}\}$ groups are exactly identical to those of the spherical $\{Mo_{132}\}$ type Keplerate [1e], the $\{Mo_{10}\}$ units are only identical to a fragment of the wheel type cluster C_s $\{Mo_{11}\}$ unit, i.e. the fragment without the 11th octahedron which is displaced. The Blue Lemon type cluster anion shows a combination of the central spherical shaped fragment with D_{8d} symmetry $\{Mo_{288}\}(\equiv\{Mo_{288}O_{784}(H_2O)_{192}(SO_4)_{32}\})$ and two capping fragments $\{Mo_{40}\}(\equiv\{Mo_{40}O_{124}(H_2O)_{24}(SO_4)_8\})$ with C_{4v} symmetry. The average reduction state of the two $\{Mo_{40}V\}$ type caps is *lower* than that of the spherical central $\{Mo_{288}\}$ fragment. This observation is in accordance with the model proposed above, that growth processes in

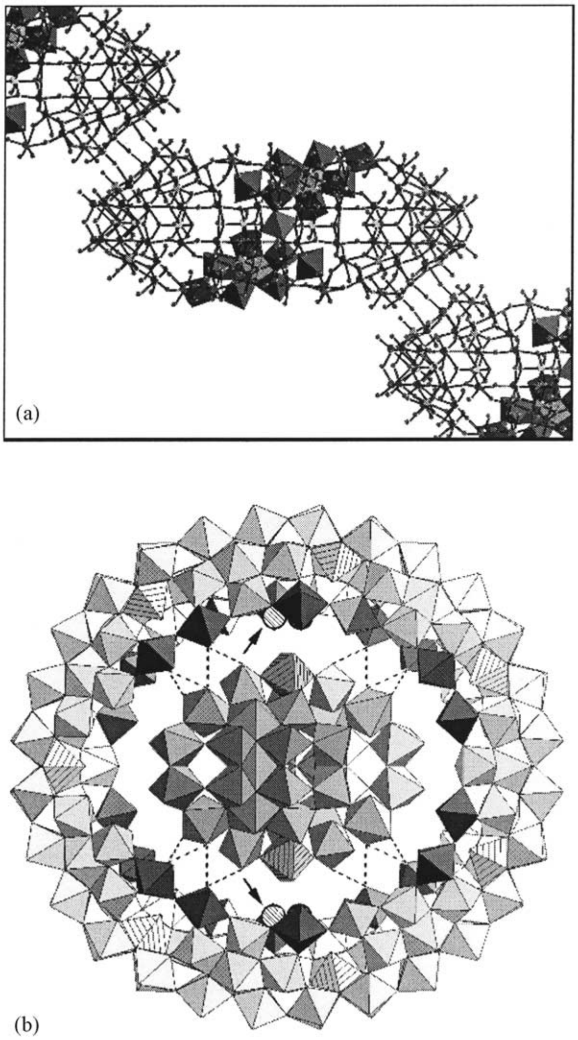


Fig. 14. Structural details of the novel supramolecular system of the type $\{Mo_{36} \subset Mo_{148}\}$ (guest occupation of the cavities: ca. 20%). (a) Part of the chain structure, which is built up by linking ring-shaped $\{Mo_{148}\}$ cluster units (i.e. based on the $\{Mo_{154}\}$ type with three 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 with O (host)$\cdots$O (guest) $= 2.744$–2.965 Å) and (at least) four sodium cations situated between host and guest (indicated by arrows, only two Na positions are visible in this perspective view). The sodium salt crystallizes in the space group $C2/m$ ($a = 29.425$, $b = 51.078$, $c = 30.665$ Å, $\beta = 114.85°$). The aspect of general interest: The $\{Mo_{36}\}$ cluster, which is the only species in highly acidified aqueous molybdate solution before the reducing agent is added, acts usually as a template for the generation of the giant wheel. (A. Müller et al., unpublished)

polyoxomolybdate systems are mostly based on nucleophiles which start 'growing' by directing the formation of electrophiles (in a relative consideration) with which they get capped. In the present case, the more nucleophilic central part probably directs the formation of the electrophilic type units with which it gets capped. As mentioned earlier, we observed that the nucleophilic ε-Keggin type derivative $\{Mo_{16}\}$ moiety directs the growth and gets asymmetrically capped by $\{Mo_{10}\}$ and $\{Mo_{11}\}$ and a $\{Mo_{57}V_6\}$ cluster under reducing conditions takes up six electrophilic $\{MoO\}^{4+}$ to form the $\{Mo_{63}V_6\}$ species (Fig. 1) [6].

The presence of sulfate ligands in the $\{Mo_{368}\}$ cluster also plays a very significant role. The negative charge in the present case is supported by the abundance of SO_4^{2-} ligands coordinated both to the intermediates and to the final cluster species. This situation does not occur in presence of much weaker coordinating ligands, such as Cl^- or ClO_4^- ions. In cases where $HClO_4$ or HCl are used as acidification agents instead of H_2SO_4 not the $\{Mo_{368}\}$ cluster but pure molybdenum-oxide based wheel type species like $\{Mo_{176}\}$ are formed. For the present purpose it is important to note that the coordination ability of the SO_4^{2-} is not too strong (e.g. as it would be in the case of PO_4^{3-} coordinating to all fragments and thus a coordination flexibility is guaranteed with the consequence that a variety of different appropriate building blocks with and without sulfate can be generated [2].

6. Materials science aspects and perspectives for nanochemistry with giant polyoxomolybdates

The chemist, according to Lehn, '*engraves into matter the products of creative imagination [. . .] creates original molecules, new materials and [. . .] indeed entire new worlds, that did not exist before they were shaped at the hands of the chemist, like matter is shaped by the hand of the artist [. . .]*' [14a]. Polyoxometalate chemists, between artistic creativity and chemical ingenuity, endeavour to understand the emergence of complexity in these molybdenum-oxide systems under reducing conditions, for example in comparison to the polyoxotungstate situation where the variety of giant clusters does not exist (see Refs. [2,27,28]). Reasons for this phenomenon have been mentioned in Ref. [2]. Beyond their beauty, the reported clusters mark the least understood zone of material complexity—the mesoscopic arena—where molecular properties start taking the 'back-seat' giving way to the emergence of bulk properties of matter.

Having unraveled the mystery of molybdenum blue containing the flexible pentagonal building blocks, we can now implement our knowledge to construct novel, revolutionary materials, with far-reaching consequences. The creation of such well-defined novel molybdenum-oxide based nanoobjects, e.g. wheel- and spherical-shaped species with large central cavities and sizable pores, can be considered as a starting point of a unique nanochemistry.

The reported clusters are interesting for materials science aspects because of their (large) *size, solubility, stability, giant cavities, nanosized changeable pores, unique surfaces, (interesting) electronic structures, and abundance of magnetic centres in a huge variety of topologies*. Moreover these clusters can be manipulated keeping the robust skeleton intact. Encapsulation of giant clusters with

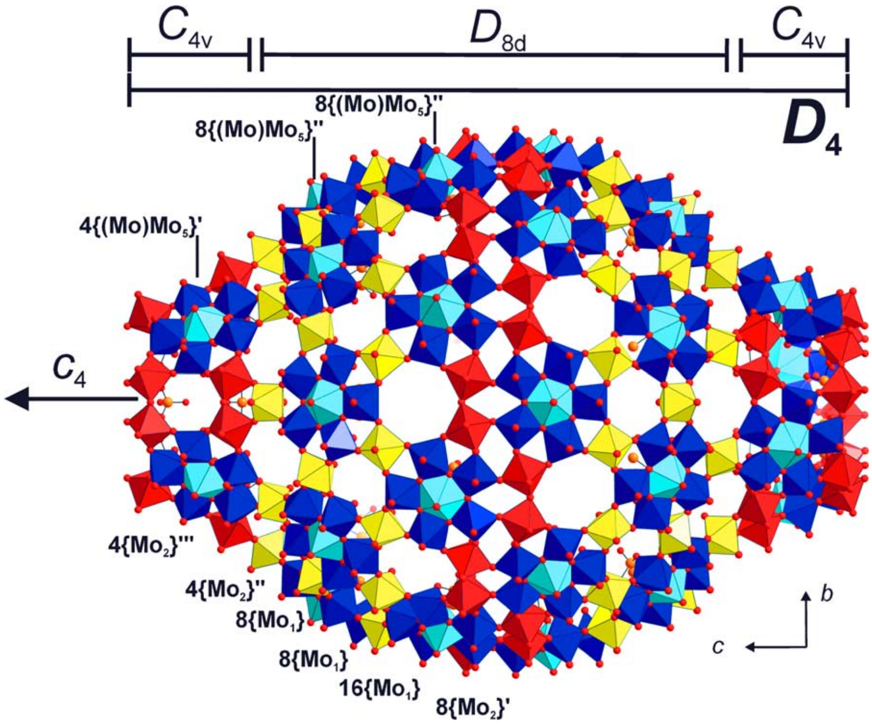


Fig. 15. $[H_xMo_{368}O_{1032}(H_2O)_{240}(SO_4)_{48}]^{48-}$ cluster anion in polyhedral representation showing the different building blocks and large areas of different local symmetry.

surfactant molecules also allows to produce LB films or even assemble organic–inorganic hybrid materials layer by layer. For instance, $\{Mo_{132}\}$ type spherical nanoclusters were embedded in a microporous silica matrix to produce a $\{Mo_{132}\}$-silica hybrid type material with porous network providing commensurate passage only for some specific substrates and allowing leaching of Mo from the pockets of 'frozen solution' of silica network. This enabled the investigators to perform specific reactions within these pockets that can be monitored for example by SAXS and UV–vis, spectroscopy [4f]. Novel, stable supramolecular architectures were obtained by encapsulating smaller $\{Mo_{57}V_6\}$ and even larger $\{Mo_{132}\}$ type clusters with cationic surfactants [4a,4b,4c,4d,4e]. Employing the technique of cationic

Table 1
Nanoscaled polyoxometalate clusters for materials science problems

Topics/keywords	Characteristics	References
LB films	Based on encapsulation of $\{Mo_{132}\}$ with cationic surfactants	[4c]
Monolayers	Based on encapsulation of $\{Mo_{132}\}$ with cationic surfactants	[4c]
Liquid crystals	Based on encapsulation of $\{Mo_{154}\}$ with cationic surfactants	[4g]
Hybrid materials with silica and carbon tubes	Based on integration of $\{Mo_{154}\}$ and $\{Mo_{132}\}$ clusters	[4f,4h]
Nanoporous clusters with cavities	Spherical-shaped clusters with pores are highly selective for cations and allow the incorporation of interesting clusters and important aggregates, for example of water molecules including those[a] with electrolytes	[15,22,30,31][a]
Nanoreactors	Wheel-shaped clusters show functionalities and especially nucleation processes inside their central nanoscaled cavity	[1b,1c],[b]
Soft matter: aggregates, vesicles, colloids	Giant clusters show hierarchic patterning in solution and lead to a new type of vesicles	[5]
Clusters as magnets	$\{Mo_{75}V^{IV}_{20}\}$ with 10 V^{IV} triangles linked $\{Mo_{72}Fe^{III}_{30}\}$ is a model for a classical magnet $\{V^{IV}_{15}\}$ shows a layered magnetic structure	[4i,8],[c]

[a] M. Gross, Encapsulation Chemistry, Chem. in Britain 39 (2003) August issue (in press).

[b] A. Müller, SQ.N. Shah, H. Bögge, M. Schmidtmann, Nature 397 (1999) 48.

[c] D. Gatteschi, L. Pardi, A.L. Barra, A. Müller, Nature 354 (1991) 463. Several sophisticated physical studies have been published about the V_{15} clusters, for example: I. Chiorescu, W. Wernsdorfer, A. Müller, H. Bögge, B. Barbara, Phys. Rev. Lett. 84 (2000) 3454; B. Barbara, I. Chiorescu, W. Wernsdorfer, H. Bögge, A. Müller, Progr. Theor. Phys. Suppl. 145 (2002) 35 as well as literature cited therein.

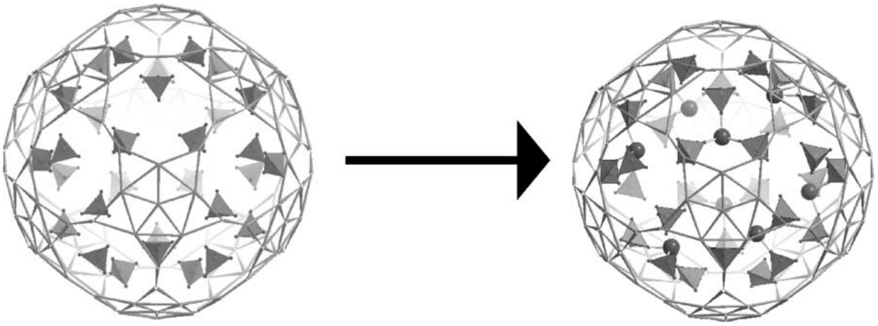


Fig. 16. pH controlled nucleation in nanoscaled cluster cavities. The anion of the type $[\{(Mo^{VI})Mo^{VI}_5\}_{12}\{L\}_{30}]$ with L = phosphate (grey tetrahedra) shows—in presence of molybdate in solution and by lowering the pH nearly to 2—a 'nucleation' process inside the cluster cavities (new $\{MoO_3\}$ units grey spheres).

surfactant encapsulation [4a] some investigators even succeeded in producing extended disk-shaped liquid-crystals that is, like organic–inorganic hybrid materials with the wheel-shaped $\{Mo_{154}\}$ anion forming the inorganic core [4g]. A summary of such different results of interest for materials science are presented in Table 1.

One fascinating point refers also to the possibility of using available cavities, for example to perform reactions within these at well-defined sites (which might be hydrophilic or hydrophobic), an example being the reaction of $[\{(Mo^{VI})Mo^{VI}_5\}_{12}\{L\}_{30}]^{42-}$ $(L = \{Mo_2O_4(CH_3COO)\}^{+})$ with phosphate at different pH values: after replacement of the acetate ligand the cluster shows a pH dependent nucleation process with the formation of P–O–Mo bonds, a situation comparable to the formation of the $[PMo_{12}O_{40}]^{3-}$ Keggin anion [29] (see also Fig. 16).

Moreover, the spherical clusters which can encapsulate water molecules may present completely new perspectives for understanding more about a very common compound—water! How does a large water assembly behave when encapsulated inside a cavity [30]? Investigation of this problem will provide us with more evidence about the mystery of the structure of liquid water [31] (see also [30]), a problem which has fascinated mankind since the dawn of history.

Polyoxometalate chemistry has taken long strides since the first investigations of Scheele and Berzelius and today we can with renewed enthusiasm recall the words of David Bradley with new horizons in sight after the publication of the $\{Mo_{154}\}$ type cluster [32]:

'*Big wheel rolls back the molecular frontier*'.

Acknowledgements

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References

[1] (a) A. Müller, H. Reuter, S. Dillinger, Angew. Chem. Int. Ed. Engl. 34 (1995) 2328;
(b) A. Müller, C. Serain, Acc. Chem. Res. 33 (2000) 2;
(c) A. Müller, P. Kögerler, C. Kuhlmann, Chem. Commun. (1999) 1347;
(d) L. Cronin, P. Kögerler, A. Müller, J. Solid State Chem. 152 (2000) 57;
(e) A. Müller, P. Kögerler, H. Bögge, Struct. Bond. (Berlin) 96 (2000) 203;
(f) A. Müller, F. Peters, M.T. Pope, D. Gatteschi, Chem. Rev. 98 (1998) 239;
(g) A. Müller, S.K. Das, E. Krickemeyer, C. Kuhlmann, J. Shapley (Ed.), Inorg. Synth. 34, in press.;
(h) L. Cronin, E. Diemann, A. Müller, in: J.D. Woollins (Ed.), Inorganic Experiments, Wiley-VCH Weinheim, 2003, p. 340.

[2] A. Müller, E. Beckmann, H. Bögge, M. Schmidtmann, A. Dress, Angew. Chem. Int. Ed. 41 (2002) 1162.

[3] (a) T. Yamase, P.V. Prokop, Angew. Chem. Int. Ed. 41 (2002) 466;
(b) K. Eda, Y. Sato, Y. Iriki, Chem. Lett. (2002) 952;
(c) C. Jiang, Y. Wei, Q. Liu, S. Zhang, M. Shao, Y. Tang, Chem. Commun. (1998) 1937;
(d) W. Yang, C. Lu, X. Lin, S. Wang, H. Zhuang, Inorg. Chem. Commun. 4 (2001) 245.

[4] (a) D.G. Kurth, P. Lehmann, D. Volkmer, H. Cölfen, M.J. Koop, A. Müller, A. Du Chesne, Chem. Eur. J. 6 (2000) 385;
(b) D.G. Kurth, D. Volkmer, M. Ruttorf, B. Richter, A. Müller, Chem. Mater. 12 (2000) 2829;
(c) D.G. Kurth, P. Lehmann, D. Volkmer, A. Müller, D. Schwahn, J. Chem. Soc. Dalton Trans. (2000) 3989;
(d) F. Caruso, D.G. Kurth, D. Volkmer, M.J. Koop, A. Müller, Langmuir 14 (1998) 3462;
(e) D. Volkmer, A. Du Chesne, D.G. Kurth, H. Schnablegger, P. Lehmann, M.J. Koop, A. Müller, J. Am. Chem. Soc. 122 (2000) 1995;
(f) S. Polarz, B. Smarsly, C. Göltner, M. Antonietti, Adv. Mater. 12 (2000) 1503;
(g) S. Polarz, B. Smarsly, M. Antonietti, Chem. Phys. Chem. 2 (2001) 457;
(h) L. An, J.M. Owens, L.E. McNeil, J. Liu, J. Am. Chem. Soc. 124 (2002) 13688;
(i) D. Gatteschi, L. Pardi, A.L. Barra, A. Müller, J. Döring, Nature 354 (1991) 463.

[5] (a) A. Müller, E. Diemann, C. Kuhlmann, W. Eimer, C. Serain, T. Tak, A. Knöchel, P.K. Pranzas, Chem. Commun. (2001) 1928;
(b) T. Liu, J. Am. Chem. Soc. 124 (2002) 10942;
(c) T. Liu, J. Am. Chem. Soc. 125 (2003) 312;

(d) See also: T. Liu, E. Diemann, A. Dress, A. Müller, Nature, submitted for publication.

[6] A. Müller, J. Meyer, E. Krickemeyer, C. Beugholt, H. Bögge, F. Peters, M. Schmidtmann, P. Kögerler, M.J. Koop, Chem. Eur. J. 4 (1998) 1000.

[7] (a) M.T. Pope, A. Müller, Angew. Chem. Int. Ed. Engl. 30 (1991) 34;
(b) M.I. Khan, A. Müller, S. Dillinger, H. Bögge, Q. Chen, J. Zubieta, Angew. Chem. Int. Ed. 32 (1993) 1780;
(c) A. Müller, S. Dillinger, E. Krickemeyer, H. Bögge, W. Plass, A. Stammler, R.C. Haushalter, Z. Naturforsch. B 52 (1997) 1301;
(d) P. Mialane, A. Dolbecq, L. Lisnard, A. Mallard, J. Marrot, F. Sécheresse, Angew. Chem. Int. Ed. 41 (2002) 2398.

[8] (a) A. Müller, S. Sarkar, S.Q.N. Shah, H. Bögge, M. Schmidtmann, Sh. Sarkar, P. Kögerler, B. Hauptfleisch, A.X. Trautwein, V. Schünemann, Angew. Chem. Int. Ed. 38 (1999) 3238;
(b) A. Müller, M. Luban, C. Schröder, R. Modler, P. Kögerler, M. Axenovich, J. Schnack, P. Canfield, S. Bud‘ko, N. Harrison, Chem. Phys. Chem. (Concepts) 2 (2001) 517;
(c) D. Gatteschi, R. Sessoli, A. Müller, P. Kögerler, M.T. Pope, A. Müller (Eds.), Polyoxometalate Chemistry: from Topology via Self-Assembly to Applications , Kluwer, Dordrecht, 2001, p. 319.

[9] A. Müller, S.Q.N. Shah, H. Bögge, M. Schmidtmann, P. Kögerler, B. Hauptfleisch, S. Leiding, K. Wittler, Angew. Chem. Int. Ed. 39 (2000) 1614.

[10] A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann, F. Peters, Angew. Chem. Int. Ed. 37 (1998) 3359.

[11] (a) J. Kepler, Mysterium Cosmographicum, 1593 (see also: M. Kemp, Nature 393 (1998) 123).;
(b) A. Müller, P. Kögerler, A.W.M. Dress, Coord. Chem. Rev. 222 (2001) 193.

[12] (a) A. Müller, E. Krickemeyer, S.K. Das, P. Kögerler, S. Sarkar, H. Bögge, M. Schmidtmann, Sh. Sarkar, Angew. Chem. Int. Ed. 39 (2000) 1612;
(b) A Müller et al., Solid State Science 2 (2000) 847.

[13] A. Müller, S.K. Das, M. Talismanova, H. Bögge, P. Kögerler, M. Schmidtmann, S. Talismanov, M. Luban, E. Krickemeyer, Angew. Chem. Int. Ed. 41 (2002) 579.

[14] (a) J.-M. Lehn, Supramolecular Chemistry, Concepts and Perspectives, VCH, Weinheim 1995;
(b) J.W. Steed, J.L. Atwood, Supramolecular Chemistry, Wiley, New York, 2000;
(c) F. Vögtle, Supramolecular Chemistry, Wiley, New York, 1991.

[15] A. Müller, S.K. Das, P. Kögerler, H. Bögge, M. Schmidtmann, A.X. Trautwein, V. Schünemann, E. Krickemeyer, W. Preetz, Angew. Chem. Int. Ed. 39 (2000) 3413.

[16] (a) A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann, C. Beugholt, S.K. Das, F. Peters, Chem. Eur. J. 5 (1999) 1496;
(b) A. Müller, M. Koop, H. Bögge, M. Schmidtmann, C. Beugholt, Chem. Commun. (1998) 1501.

[17] A. Müller, E. Beckmann, H. Bögge, M. Schmidtmann, Inorg. Chem. Commun., to be submitted for publication.

[18] A. Müller, C. Beugholt, M. Koop, S.K. Das, M. Schmidtmann, H. Bögge, Z. Anorg. Allg. Chem. 625 (1999) 1960.

[19] A. Müller, R. Maiti, M. Schmidtmann, H. Bögge, S.K. Das, W. Zhang, Chem. Commun. (2001) 2126.

[20] A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann, P. Kögerler, C. Rosu, E. Beckmann, Angew. Chem. Int. Ed. 40 (2001) 4034.

[21] A. Müller, L. Toma, H. Bögge, M. Schmidtmann, Chem. Comm. 2003, 2000.

[22] A. Müller, B. Botar, H. Bögge, P. Kögerler, A. Berkle, Chem. Commun. (2002) 2944.

[23] A. Müller, C. Beugholt, H. Bögge, M. Schmidtmann, Inorg. Chem. 39 (2000) 3112.

[24] L. Cronin, C. Beugholt, E. Krickemeyer, M. Schmidtmann, H. Bögge, P. Kögerler, T.K.K. Luong, A. Müller, Angew. Chem. Int. Ed. 41 (2002) 2805.

[25] A. Müller, S. Roy, M. Schmidtmann, H. Bögge, Chem. Commun. (2002) 2000.

[26] P. Ball, Nature Homepage, Materials Update, April 25 (2002).

[27] K. Wassermann, M.H. Dickman, M.T. Pope, Angew. Chem. Int. Ed. 37 (1997) 1445.

[28] U. Kortz, M.G. Savelieff, B.S. Bassil, M.H. Dickman, Angew. Chem. Int. Ed. 40 (2001) 3384.

[29] A. Müller, S.K. Das, E. Beckmann, unpublished results.

[30] A. Müller, H. Bögge, E. Diemann, Inorg. Chem. Commun. 6 (2003) 52.

[31] (a) M. Henry, Chem. Phys. Chem. 3 (2002) 607;
(b) A. Müller, M. Henry, Angew. Chem. (to be published).

[32] D. Bradley, New Scientist 148 (1995) 18.