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Oxomolybdates: From Structures to Functions
in a New Era of Nanochemistry
Achim Müller and Soumyajit Roy

Abstract

From a unique library containing the molybdenum-oxide based building blocks/fragments under reducing conditions in aqueous solution a huge variety of nano-objects, 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-wheels of the type \( \{\text{Mo}_{154}\} \) and \( \{\text{Mo}_{176}\} \) and the spherical big-balls of the type \( \{\text{Mo}_{132}\} \) and their derivatives. These are considered here in connection with the by far the largest structurally well-characterized cluster \( \{\text{Mo}_{368}\} \), which contains besides the 368 molybdenum atoms nearly 2000 non-hydrogen atoms, shows positive and negative curvatures, and has the size of hemoglobin and the shape of a lemon. A most recent achievement regarding a unique ‘nanosponge’-behaviour of the spherical clusters showing responsive sensing opens new eras of nanochemistry: nano-spherical-surface, nano-porous-cluster, and nano-super-supramolecular chemistry. Historically speaking, after solving the mystery of molybdenum blue solutions, from which the wheel type clusters can be isolated, it became evident that the acquired knowledge could be useful for advancing the frontiers of materials science. Some general aspects of the corresponding chemistry are reviewed here.

14.1
Introduction: Similarities between Nanotechnology in Nature and Chemistry?

*Der chemische Prozeß ist das ‘Höchste, wozu die unorganische Natur gelangen kann’.*
G. W. F. Hegel [1]

Nature plays with patterns. Patterning reaches a pinnacle of elegance and intricacy in nanoscopic molecular systems, the most relevant being those found in the biosphere: the variety of specific processes of the living cell are directed by an overwhelming number of nanoscaled structures, for example by the proteins which can act as carriers, fighters, administrators, food engineers, signal receivers and transducers,
and transporters. In this context the question arises as to whether it is possible for chemists/scientists to build up systems with comparable functions that would allow us to speak of \textit{machinery en miniature} in Nature and technology. Remarkably, from aqueous solutions of molybdates under reducing conditions, a huge variety of interesting structures can be obtained which offer a unique substance library and show really remarkable functionalities, even the phenomenon of cation transport through pores and of modelling cell response. These nanoscaled systems emerge by linking well-defined preformed building blocks under the canopy of self-assembly processes, which are unique regarding the overwhelming variety obtainable. A textbook example is the generation of the tobacco mosaic virus (TMV) in two phases [2]. In the first phase, the large protein building blocks are generated using encrypted genetic information and these in the second phase become linked to form the complete viral entity.

\subsection*{14.2 Sizes, Shapes, and Complexity of Nano-objects are Determined by the Nature and Variety of the Constituent Building Blocks}

In inorganic polyoxometalate systems, especially in solutions of molybdates under reducing conditions, a ‘virtual library’ of well-defined linkable building blocks exists, which can be connected under suitable conditions to form a plethora of sophisticated nanostructures. For instance, \textit{two or three identical well-defined building blocks} or fragments, each comprising 17 molybdenum atoms, become linked to form the two different nanostructures shown in Figure 14.1 [3a,b]. All such cluster species, emerging via self-assembly and woven from well-defined building blocks

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{Fig_14.1.png}
\caption{Two relatively large clusters with different structures formed by the same \{Mo\textsubscript{17}\} building block: Two or three of these \{Mo\textsubscript{17}\} building blocks are linked in different modes by different linkers to form different clusters.}
\end{figure}
of molybdenum and oxygen atoms, the most important of which are collected in Table 14.1, show the following characteristics:

- All listed clusters contain the fundamental pentagonal \{(\text{Mo})\text{Mo}_5\} building block, comprising a central pentagonal bipyramidal \{\text{MoO}_7\} group with six surrounding edge-sharing \{\text{MoO}_6\} octahedra. These can occur in very different environments and dictate correspondingly the overall size, symmetry, and complexity of the nano-objects.
- The units are, for example, central to the construction of spherically shaped entities with positive curvatures. (Note that even the famous so-called bucky-ball \{\text{C}_{60}\} fullerene molecule contains 12 pentagonal ‘units’.) However, for the generation of more complex patterns, including negative as well as positive curvatures, that is showing symmetry breaking, a rather large number of negative and positive vertices with polygons of different kinds, for example including heptagons, is necessary [4].

The highly symmetric \([(\text{pent})_{12}(\text{link})_{30}]\) type spherical clusters, such as the \{\text{Mo}_{132}\} type nanospheres (Figure 14.2, right), are comprised of 12 pentagonal \{(\text{Mo})\text{Mo}_5\} groups (pent) connected by 30 \{\text{Mo}_2\} groups acting as linkers (link) [3]. The cluster type \{\text{Mo}_{132}\} also has an interesting stoichiometric aspect in the sense that it can be formally written as \{\text{Mo}_{132}\} \equiv \{\text{Mo}_{11}\}_{12} \equiv \{\text{Mo}\text{Mo}_2\text{Mo}_5\}_{12} [5] (see below). The number twelve, an emblem of icosahedral symmetry, is significant in the context of two Platonic solids: the icosahedron and dodecahedron, the latter having 12 faces, the former 12 vertices. Interestingly, the aforementioned \{\text{Mo}_{11}\} unit, like its smaller counterpart \{(\text{Mo})\text{Mo}_5\}, also shows a five-fold symmetry axis which is necessary for the construction of spherical entities with icosahedral symmetry, be it a \{\text{Mo}_{11}\} type nanosphere or a spherical virus. The presence of the related 14 and 16 \{\text{Mo}_{11}\} groups in wheel-shaped \{\text{Mo}_{154}\} \equiv \{\text{Mo}_{11}\}_{14} and \{\text{Mo}_{176}\} \equiv \{\text{Mo}_{11}\}_{16} type clusters (Table 14.1), respectively, also reveals the central role of the pentagonal building blocks. The two different types of \{\text{Mo}_{11}\} building blocks can be distinguished easily as a lower symmetry (that is, \text{C}_5) is observed in the wheel-shaped clusters resulting from the displacement of one of the \{\text{MoO}_6\} octahedra (see Figures 14.3 and 14.4).

The structure of the \{\text{Mo}_{368}\} type cluster [4], the largest inorganic cluster known to date and also obtained from a special type of molybdenum blue solution, presents us with a paradigm shift with respect to symmetry breaking and changing curvatures in the nanocosmos. The phenomenon of symmetry breaking is visible at the surface due to the abundance of different large local symmetry areas as well as the presence of negative curvatures in between positive curvatures (see Figures 14.5 and 14.6). The structure of this cluster can be considered as a hybrid between the wheel- and ball-type clusters. The hybrid character is, in the terminology [5], manifested by the occurrence of 24 \text{C}_5-type \{\text{Mo}_{11}\} groups of the ball-type clusters together with the related 16 \text{C}_5-type \{\text{Mo}_{10}\} groups of the wheel-type clusters. The \{\text{Mo}_{10}\} groups correspond to the abundant \{\text{Mo}_{11}\} groups with only one \text{MoO}_6 octahedron less (see [4]).
Tab. 14.1. The nanocosmos of molybdenum oxide clusters formulated according to metal-based building blocks especially \(\{(\text{Mo})\text{Mo}_5\}\). This important unit which is found in all molybdenum-based nanoarchitectures (Figure 14.3), has a pentagonal \(\{\text{MoO}_7\}\) bipyramid in the centre while the Mo atoms in all other building blocks, like \(\{\text{Mo}_1\}\) or \(\{\text{Mo}_2\}\), have Mo in an octahedral environment. Building blocks, like \(\{\text{Mo}_3\}\), can show different ligand dispositions. (References are based mainly on our earlier reviews.)

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<th>Cluster</th>
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<th>Formulation Based on Largest Building Blocks</th>
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<td>({\text{Mo}_{40}})</td>
<td>14.8</td>
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<td>12 CH(_3)COO(^-)</td>
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<td>48 SO(_4^{2-})</td>
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* Exist with different metal centres.
** Other possible tilings: \(\{\text{Mo}_7\}_2\{\text{Mo}_1\}_2\) and \(\{\text{Mo}_1\}_2\{\text{Mo}_2\}_3\{\text{Mo}_1\}_2\).

14.2 Sizes, Shapes, and Complexity of Nano-objects are Determined by the Nature of the soluble species. Other possible counterions/ligands include Cl\(^-\) and NO\(_3\)\(^-\).
An imminent question in this context might be: what leads to the development of such positive and negative curvatures in the nanoscopic landscape of a cluster? Without doubt, the presence of a large number of building blocks in the reaction medium is a reason for the emergence of such complex architectures showing...
symmetry breaking. But still the question remains: how can such a structure be produced or how can a large number of building blocks be generated in solution? It is known that the largest cluster in acidified molybdate solution is, in the absence of a reducing agent, the “rather small” \( \{\text{Mo}_{36}\} \) type anion \([3a, 4, 6, 7]\) which starts growing under reducing conditions. (Note that this is even larger than the largest discrete silicate ion.) An increase in negative charge, due to reducing conditions, not only prevents uncontrolled linking, but also initiates further protonation which is a prerequisite for further growth \([4]\). The increase in negative charge in the present case is also supported by the abundance of \( \text{SO}_4^{2-} \) ligands coordinated to the intermediates and the final cluster species. Another important aspect is the related coordination ability: \( \text{SO}_4^{2-} \) is a moderately strong ligand and therefore favors an increase in the number of building blocks which might be coordinated or non-coordinated. In the presence of much weaker coordinating ligands, such as \( \text{Cl}^- \) or \( \text{ClO}_4^- \) ions, in cases where \( \text{HClO}_4 \) or \( \text{HCl} \) is used as acidification agent instead of \( \text{H}_2\text{SO}_4 \), the \( \{\text{Mo}_{36}\} \) cluster is not formed, “only” pure molybdenum oxide-based \( \{\text{Mo}_{154}\} \) or \( \{\text{Mo}_{176}\} \) wheel-type species without \( \text{Cl}^- \) or \( \text{ClO}_4^- \) ligands. For the present purpose it is important to note that the coordination ability of the \( \text{SO}_4^{2-} \) ligand is ideal, as it is not too strong (as would be the case for \( \text{PO}_4^{3-} \) where all units would be coordinated) and not too weak \([4]\).

14.3 Nanoscaled Clusters with Unusual Form–Function Relationships

Let us continue our tour of sophisticated nanostructures by giving some striking examples of the multifaceted form–functionality correlation principles involved. The following parent cluster types will be considered (here we refer to earlier published reviews):
Fig. 14.4. Molecular giant wheels and balls show a remarkably similar (formal) \( \{\text{Mo}_{11}\}_n \) stoichiometry: comparison of the structures of the \( \{\text{Mo}_{11}\}_{12} \) (top) and \( \{\text{Mo}_{11}\}_{16} \) clusters (middle and bottom, with side and top view, respectively). The \( \{\text{Mo}_{11}\} \) unit is highlighted in each case.
1. Wheel-shaped clusters of the type \{Mo_{154}\} and \{Mo_{176}\} \cite{3, 6} with large central cavities that can be easily modified by means of simple well-known chemical reactions (see Figure 14.4).

2. Spherical-shaped clusters of the type \[(pent)_{12}\text{(link)_{30}}\] \cite{3, 5, 8} with nanoscaled tunable cavities and large tunable pores (see Figure 14.2).

3. Torus-shaped clusters of the type \{Mo_{57}\} \cite{3a} with potential functional indentations on the cluster surface (see Figure 14.1 right).

The giant wheel molybdenum-oxide based anions can be considered as objects which show a variety of nanoscale structural functionalities ("nanostructured landscape") not only allowing reactions at a variety of well-defined centres/groups but also offering the option of acting as potential nano-reactors or -containers \cite{6, 9–12}). Some relevant reactions are:

- The substitution of H$_2$O ligands coordinated to the molybdenum centres of \{Mo$_{154}$\} by ambivalent and/or multivalent ligands, for example the amino acid cystine can be coordinated to the inner wall of the cluster cavity and hence creates hydrophobic and hydrophilic surroundings with different functionalities (see Figure 14.7) \cite{9}.
Fig. 14.6. Forms with positively and negatively curved surfaces: the sphere (top) and the outer part of a torus (bottom left) are examples of surfaces exhibiting positive curvatures, the saddle (bottom right) and the inner part of the torus (bottom left) representing negative curvatures.

Fig. 14.7. Endohedral functionalization of the inner surface of a wheel-shaped \( \{\text{Mo}_{154}\} \) type nanocluster by cystine ligands (polyhedral representation, carboxylate group in ball-and-stick).
The (larger) hexadecameric \{Mo\_{176}\} type cluster also shows a similar variety of functionalities and even a manifold of \((16 + 16)\) non-equivalent receptor sites for cations as well as anions allowing, for example, the formation of a novel supramolecular host–guest system while integrating 16 K\(^{+}\) and 16 SO\(_4^{2-}\) ions, thus leading to the formation of an unusual encapsulated 64-membered zigzag ring system (see Figure 14.8) [10].

Paramagnetic metal centres like Cu\(^{2+}\) ions can be incorporated into the cavities spanned by four O atoms and having the appropriate size, for example of the \{Mo\_{154}\}-type rings. This type of reaction can lead to the formation of nanoobjects with unique neutral magnetic properties [11].

The ‘addition’ of two neutral \{Mo\_{16}\}-type ‘hub-caps’ to the surface inside the cavity of the \{Mo\_{176}\}-type wheel leads to the formation of a \{Mo\_{248}\} cluster and corresponds to a nucleation process under boundary conditions [2a] (see Figure 14.9). This reaction can be regarded as a model for both crystal growth, especially for the related initial nucleation process, which is still not clearly understood, and also for metal-centre uptake processes in biological systems. In particular, such
growth processes might be allied to biomineralization processes in compartments. In this context the molybdenum-atom uptake of the Mo storage protein of the N₂-fixing microorganism *A. vinelandii* is worth mentioning. According to our preliminary results the inorganic nucleus corresponds to a rather large polyoxomolybdate.

- The nucleophilic \( \text{MoO}_6 \) hexagonal ring-shaped sites act as receptors for cations, for example protonated urea guests \([12b]\), a comparable situation to the above-mentioned case of the integrated \( 16 \text{K}^+ \ [10] \). In the urea case this can be used to decrease the negative charge thereby nicely facilitating chain formation \([12b]\), a fact which shows perspectives for related nano-, supramolecular-, and solid-state chemistry.

In the case of the spherical nano-objects (Table 14.1), formed by 12 pentagonal \( \{\text{MoO}_3\} \) units linked by 30 mono- or dinuclear linkers, there is, for each species, a nanoscaled capsule cavity and 20 size-tunable specific nanopores of the type \( \{\text{Mo}_n\text{O}_n\} \) (for example with \( n = 6 \) or 9), which can act as substrate specific receptors \([8]\). The cavity can even house smaller polyoxometalates, like different Keggin ions, to form a supramolecular nanocomposite of a unique kind (see Figure 14.10) \([13]\). Some other interesting reactions are:

- The replacement of the 30 diamagnetic \( \{\text{Mo}_2\} \)-type linkers of the spherical \( \{\text{Mo}_{12}\} \)-type clusters by 30 paramagnetic centres like \( \text{Fe}^{III} \) leads to the emergence of unusual molecular nanoantiferromagnets of the type \( \{\text{Mo}_{72}\text{Fe}_{30}\} \) (see Figures 14.2 and 14.11) \([14]\).

- The neutral spherical nano-objects of the type \( \{\text{Mo}_{72}\text{Fe}_{30}\} \) can be crosslinked in a solid-state reaction, even at room temperature (!), to form layers by following an elementary inorganic condensation reaction, known already for the formation of polycations like those of \( \text{Fe}^{III} \) in aqueous solution. The rapid loss of water molecules from the freshly filtered crystals, comprising discrete spheri-
cal clusters, leads to their approximation which is a condition for their co-
valent linking (see Figure 14.12) [15]. The possibility of forming a related one-
dimensional chain (paramagnetic Keplerate “necklaces”) from similar spherical
nanospheres in a room-temperature reaction also exists [16]. It is even possible to ‘kick out’, like soccer balls, the neutral giant molybdenum
oxide spheres, for example the \{Mo_{72}Fe_{30}\} ones, into the gas phase using all
matrix-assisted laser desorption and ionization (MALDI) methods. It is impor-
tant that the clusters range from dimers to pentamers (see Figure 14.13) [17].

A further fascinating point refers to the possibility of performing different types
of reactions inside the cavities of such spherical clusters at well-defined sites,
which can be hydrophilic or hydrophobic. Here we describe for the first time
an example, the details of which have, as yet, not been published: the reaction of \[\text{[\text{(MoVI)MoVI}_{5}]_{12}\{\text{L}\}_{30}}\] with phosphate and mo-
lybdate in aqueous solution at different pH values demonstrates that, after re-
placement of the acetate ligands, the cluster shows in its cavity a pH-dependent
nucleation process in the presence of molybdate. This leads to the formation of
new P–O–Mo bonds at low pH, a situation comparable to the formation of the
\[\text{[PMo}_{12}\text{O}_{40}]^{3–}\] Keggin anion at low pH values [18] (see also Figure 14.14).
Fig. 14.11. Nanomagnet as a classical magnet en miniature on the cover-page of ChemPhysChem. The \{\{\text{Mo}\text{Mo}_5\}\}_2\{\text{Fe}_{30}\}
cluster (see also Figure 14.2) in two representations, including one showing the orientation of the spins at the Fe\(^{III}\) triangles was, because of its unusual properties, studied at very low temperature (there it still behaves as a classical antiferromagnet) and extremely high magnetic field strength.
All these spherical clusters can be described, as mentioned above, as \[\{(Mo)Mo_5\}_{12}\{(Fe^{III})\}_{10}\]. It was suggested to call them ‘Keplerates’ because of their striking similarity to a fragment of Kepler’s early speculative model of the universe, as described in his opus *Mysterium Cosmographicum* (see Figure 14.15). The related Keplerate type chemistry is especially interesting for mathematicians [3c]. Furthermore, these clusters also show, topologically speaking, a similarity to spherical viruses (Figure 14.16).

**Fig. 14.12.** Crosslinking neutral spherical nanoclusters of the type \[\{(Mo)Mo_5\}_{12}\{(Fe^{III})\}_{10}\], indicated by two FeO6 octahedra sharing corners, leads to the formation of a layered structure based on an unusual solid-state reaction at room temperature.

14.4 Perspectives for Materials Science and Nanotechnology: En Route to Spherical-Surface, Nanoporous-Cluster, and Super-Supramolecular Chemistry including the Option of Modelling Cell Response

The clusters described above are interesting for materials science and nanotechnology aspects because of their stability, size, solubility (in several solvents), giant
Fig. 14.13. Unique nanocluster aggregates in the gas phase: MALDI mass spectra of the neutral clusters of the type \{Mo_{72}Fe_{30}\} and \{Mo_{102}\} and their oligomers.

Fig. 14.14. pH controlled nucleation in nanoscaled cluster cavities: the anion \([\left\{(\text{MoVI})\text{MoVI}_{5}\right\}_{12}L_{10}\] with \(L = \text{phosphate}\) (gray tetrahedra left) shows in the presence of molybdate in solution and by lowering the pH to nearly 2 a ‘nucleation’ process inside the cluster cavities with the formation of P-O-Mo bonds (\{MoO\right\}_{x} units gray spheres).
Fig. 14.15. Nano- and macrocosmos/universe similarities: schematic representation of the \{Mo_{132}\} type cluster on the cover-page of *Angew. Chem.*, highlighting its similarity to Kepler’s early model of the universe and “abundance” of related icosahedra in both cases. Important: it was the starting point for the consideration of Keplerate type nanochemistry from a topological point of view (see [3c]).
cavities, ‘nanosized’ changeable pores, unique surfaces, unusual electronic structures, and last but not least abundance of magnetic centres in a variety of topologies. Moreover, most of the clusters, especially the spherical ones, can be manipulated whilst keeping the robust nanoscopic oxomolybdate skeleton intact. Encapsulation of the giant clusters with surfactant molecules allows one to produce LB films and monolayers. Some of these even form a new type of vesicle with the option of getting information about the structure of liquid water. A summary of these and other relevant aspects is presented in Table 14.2; for further details see the collection of papers in [19].

A recent challenge in nanotechnology is to mimic the material constructions and molecular-recognition-type responsive sensing of biological systems. Intracellular response to extracellular signals involves signal transduction via molecular recognition of the specific receptors on the cell surface, which can trigger enzymatic reactions in the cell. Such a “cognitive isomorphism” on a molecular level, a rare phenomenon in classical chemistry, is, for example, of immense importance for understanding the complex dynamics of ‘uptake and release’ of substrates in general.

The nanoball of the type \{Mo_{132}\} shows such molecule-response activity. It can be compared to a ‘nanosponge’ with a multitude of open pores accessible for a specific substrate, for example, guanidinium cation guests in the case of \{Mo_{132}\}. 

Fig. 14.16. Nanoscaled systems of the biosphere and of chemistry show the same topology: schematic representation of the icosahedron spanned by the 12 centres of the \{(Mo)Mo_5\} units of the \{Mo_{112}\} type cluster (a) and of the satellite tobacco necrosis virus (STNV) with the triangulation number $T = 1$ (see for example [3a]) highlighting one of the 60 protomers (dark gray) (b). Two \{Mo_{11}\} units in (a), each formed by the \{(Mo)Mo_5\} groups and the five related Mo centres of the five neighbouring \{Mo^5\_O_4\}^{2+} linkers, are highlighted.
The suction of substrates into this ‘nanosponge’, while simultaneously closing the pores, essentially triggers a restructuring of the incarcerated solvent molecules, a situation comparable to the mentioned intracellular response to an extracellular stimulus. Moreover, as different types of substrates can interact with different types of pores on a specific spherical nanosurface, the situation might be noted as the beginning of an era of nanoscaled spherical-surface chemistry. Additionally, since the pore sizes of the clusters can be varied and show corre-

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<td>Liquid crystals</td>
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<td>Nanoporous clusters with cavities</td>
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<td>Nanoreactors</td>
<td>Wheel-shaped clusters show functionalities and especially nucleation processes inside their central nanoscaled cavity</td>
<td>3a**</td>
</tr>
<tr>
<td>Soft matter: aggregates, vesicles, colloids</td>
<td>Giant clusters show hierarchic patterning in solution and lead to a new type of vesicles</td>
<td>19i, 19k, 19l</td>
</tr>
<tr>
<td>Clusters as magnets</td>
<td>{Mo_{75}V^{III}<em>{20}} with 10 V^{IV} triangles linked {Mo</em>{72}Fe^{III}<em>{30}} is a model for a classical magnet {V^{IV}</em>{15}} shows a layered magnetic structure</td>
<td>3a, 8c, 14***</td>
</tr>
</tbody>
</table>


***Several sophisticated physical studies have been published of the V_{15} cluster have been published, for example: I. Chiorescu, W. Wernsdorfer, A. Müller et al., Butterfly Hysteresis Loop and Dissipative Spin Reversal in the S = 1/2, V_{15} Molecular Complex, Phys. Rev. Lett. 2000, 84, 3454–3457; B. Barbara, I. Chiorescu, W. Wernsdorfer et al., The V_{15} Molecule, a Multi-Spin Two-Level System: Adiabatic LZS Transition with or without Dissipation and Kramers Theorem, Progr. Theor. Phys. Suppl. 2002, 145, 357–369.
spondingly different reactivities, we can also refer to a nanoporous-cluster chemistry and, because of the large number of receptors involved (20 in the case of icosahedral spheres), to a super-supramolecular chemistry. In this connection recent unpublished $^1$H NMR investigations have revealed that the uptake and release of 'guanidinium' substrates in solution by the 'nanosponge' shows an interesting temperature dependence corresponding to an open-and-shut process [20].

An aspect of particular relevance refers to the exciting problem of the structure of liquid water. The closing of the cluster’s ‘nanowindow’ leads, in the case of the \{Mo$_{132}$\} cluster, to the reorganization of the internal H$_2$O molecules into a giant and structurally well-defined (H$_2$O)$_{100}$ cluster which can be considered as a snapshot of liquid water (see [8, 21] and Figures 14.18 and 14.19). (The endohedral clusterization of water molecules upon substrate uptake into the pores formally corresponds to the cellular response to an extracellular stimulus on the cell surface.) Our special endohedral clusterization of water molecules would certainly have pleased both Plato and Archimedes as the water cluster can be formally (!) arranged in shells showing a larger and smaller dodecahedron, each composed of a (H$_2$O)$_{20}$ segment and one rhombicosidodecahedron (H$_2$O)$_{60}$ [8, 21]. This example shows that with the present nanocontainers, available for the encapsulation of segments of different kinds of (macroscopic) substances and even rather large molecular systems, problems of tremendous importance for contemporary science can be solved. Even the liquid water problem which has been characterized as “The most important problem in science that hardly anyone wants to solve” [22]. Now we deny this statement.

Fig. 14.17. The 20 pores of a spherical nanocluster of the type \{Mo$_{132}$\} can be closed through substrate uptake. Right: one \{Mo$_9$O$_8$\} pore in ball-and-stick representation (PO$_2$H$_2$$^-$/SO$_2$$_2^-$ ligands shown as tetrahedra). Left: space-filling model of the cluster with inserted guanidinium cations (only CN$_3$ part shown). Closing the pores leads to a structural reorganization of the encapsulated water molecules.
Fig. 14.18. A nanodrop of water found in the cavity of a $\{\text{Mo}_{132}\}$ cluster (top) and the hierarchical structure of the $(\text{H}_2\text{O})_{100}$ assembly showing two Platonic (a larger and a smaller $(\text{H}_2\text{O})_{20}$ dodecahedron) and one $(\text{H}_2\text{O})_{100}$ Archimedean solid in a formal consideration (middle). One tetrahedrally coordinated O atom as in liquid water is also emphasized (bottom).
Fig. 14.19. A result of modern nanochemistry: Plato and Archimedes look pleased viewing the nanodrop of water \( \{H_2O\}_{100} \) inside a molybdenum-oxide ‘nanosponge’ occurring (formally) in the form of shells, that is two \( \{H_2O\}_{20} \) dodecahedra and a rhombicosidodecahedron \( \{H_2O\}_{60} \). Note, as in liquid water all O \( \cdots \) O distances are of the order of 2.7 Å.
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