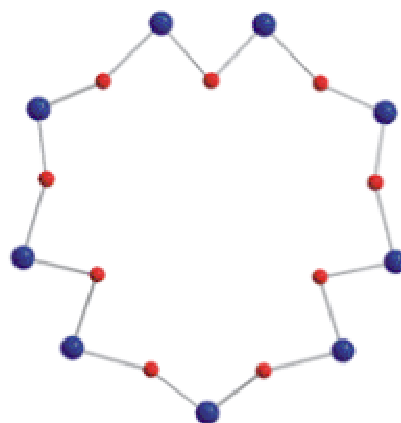
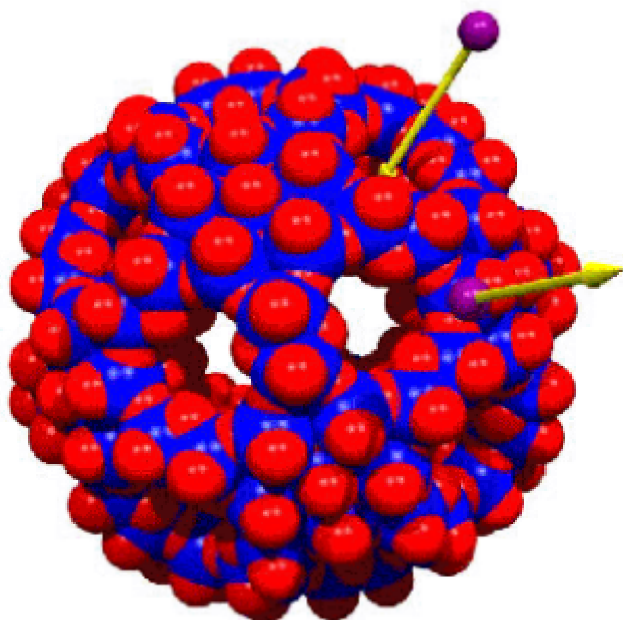


The information below highlights one of the group of AM's key continuing research projects, and is presently the main one. For authors' names of the given papers, see list of publications. Some earlier reviews on basic chemistry:

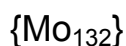
- **"Polyoxometalate Chemistry: An Old Field with New Dimensions in Several Disciplines"**, Angew. Chem. Int. Ed. Engl. 30, 34-48 (1991)
- **"A variety of combinatorially linkable units as disposition: from a giant icosahedral Keplerate to multi-functional metal-oxide based network structures"**, Chem. Comm. 1347-1358 (1999)
- **"Polyoxometalates: Very Large Clusters - Nanoscale Magnets"**, Chem. Rev. 98, 239-271 (1998)
- **"A variety of combinatorially linkable units as disposition: from a giant icosahedral Keplerate to multi-functional metal-oxide based network structures"**, Chem. Comm. 1347-1358 (1999)
- **"Soluble Molybdenum Blues - 'des Pudels Kern'"**, Acc. Chem. Res. 33, 2-10 (2000)

In the below listed original papers, it was argued that only the molybdate system allows the described versatile chemistry.

From Porous Capsules/Artificial Cells to Sphere Surface and Super-Supramolecular Chemistry: Perspectives for Chemistry under Confined Conditions, Artificial Cell Environment Interactions as well as Nanotechnology



One of the 20 Mo₉O₉ pores with crown ether function



Structurally well-defined porous spherical metal-oxide based nanocapsules/artificial cells of the type {Pentagon}₁₂{Linker}₃₀ allow unprecedented chemistry (Figure). The area shows revolutionary routes to *different disciplines*, like **chemistry** (e.g. modelling passive ion

transport through membranes), **materials science** (e.g. construction of a nano ion chromatograph), **physics** (especially regarding confined matter properties), and **mathematics** (concerning the tiling problem of spherical surfaces).

This is based on the following related facts:

1. the size of the capsules and their pores/channels can be tuned, while the latter can be opened and shut,
2. the internal cavity's shell functionality can be tuned, e.g. from hydrophilic to hydrophobic, and
3. the twenty(!) abundant pores of the nanosponge have crown-ether functions with respect to cations allowing *sphere-surface* as well as *super-supramolecular chemistry* including in principle the study of allosteric effects.

Options for the following basic/new type of research topics are evident:

1. *Encapsulation Chemistry*: This refers to studies of encapsulated nanomaterials of different types - including water with and without electrolytes - taken up through capsule pores. The capsules themselves can separate/position cations like a nano ion chromatograph in the sense of structure directed vectorial-type translocations.
2. *Capsule-Coordination Chemistry*: This allows a new type of spectroscopic and magnetic studies of encapsulated discrete/shielded mono- and polynuclear complexes, while encapsulated water shells can act as polydentate ligands.
3. *Artificial Cell Environment Interactions*: In this respect some of *Nature's* pathways can be modelled, like ion uptake-and-release processes (Figure) as well as cell response to stimuli, since pore closing by molecules like corks - formally considered as "stimuli" - influences significantly encapsulates' (like water) structures; this refers to confined condition phase transfer. Generally speaking, model cell environment interactions can be studied on a wide range.

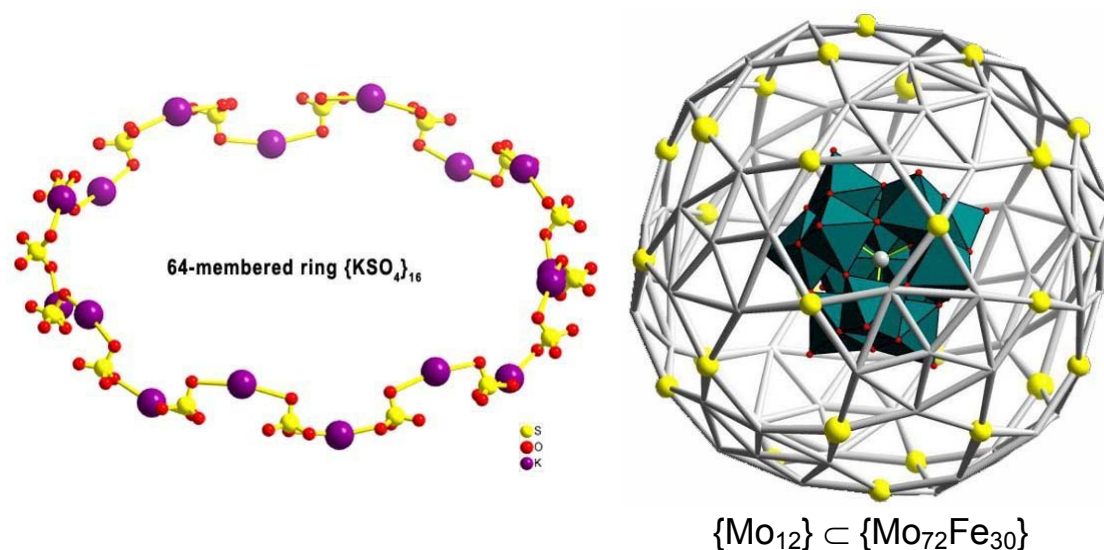
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- **"Artificial Cells: Temperature-Dependent Reversible Li⁺-Ion Uptake/Release Equilibrium at Metal Oxide Nanocontainer-Pores"**, *Angew. Chem. Int. Ed.* 43, 4466-4470 (2004); Corrigendum: 43, 5115
 - **"En route to coordination chemistry under confined conditions in a porous capsule: Pr³⁺ with different coordination shells"**, *Chem. Comm.* 2038-2039 (2004)
 - **"Drawing Small Cations into Highly Charged Porous Nanocontainers Reveals "Water" Assembly and Related Interaction Problems"**, *Angew. Chem. Int. Ed.* 42, 2085-2090 (2003)
 - **"Trapping Cations in Specific Positions in Tuneable "Artificial Cell" Channels: New Nanochemistry Perspectives"**, *Angew. Chem. Int. Ed.* 42, 5039-5044 (2003)
 - **"Changeable Pore Sizes Allowing Effective and Specific Recognition by a Molybdenum-Oxide-Based "Nanosponge": En Route to Sphere-Surface and Nanoporous-Cluster Chemistry"**, *Angew. Chem. Int. Ed.* 41, 3604-3609 (2002)
 - **"Thirty Electrons "Trapped" in a Spherical Matrix: A Molybdenum Oxide-Based Nanostructured Keplerate Reduced by 36 Electrons"**, *Angew. Chem. Int. Ed. Engl.* 39, 1614-1616 (2000)

- **"Archimedean Synthesis and Magic Numbers: "Sizing" Giant Molybdenum-Oxide-Based Molecular Spheres of the Keplerate Type"**, *Angew. Chem. Int. Ed. Engl.* 38, 3238-3241 (1999)

Highlighted, e.g. in:

- W. G. Klemperer, G. Westwood, "Traps for Cations", *Nature Materials (News & Views)* 2003, 2, 780.
- M. Gross, "Encapsulating Chemistry", *Chemistry in Britain* 2003, Aug. Issue, p. 18.
- N. Hall, "Bringing Inorganic Chemistry to Life", *Chemical Communications* 2003, 803.
- F. Frick, "Das Zauberreich der Moleküle" (with cover picture), *Bild der Wissenschaft* 03/2003, 76-98.
- R. Kurschat, "Synthese eines gastfreundlichen Molekülclusters - Erster Schritt zu einer "super-supramolekularen" Chemie", *Neue Zürcher Zeitung*, 13.11.2002.
- "Molibdeno con sorpresa", *El Pais (Spain)*, 6. January 1999.

Nanoscaled Objects: Characteristic Internal and External Surface Functionalities Show Routes for a New Type of Chemistry



Nanoscaled species with well-defined surface-structured landscapes have properties unknown for small molecules and can give rise (if they can be dissolved) to a versatile chemistry depending on their special type of surface functionalities as well as on their molecular shapes. In the present case this refers to two important consequential(!) forms, the spherical hollow- and wheel-type kind.

Options include:

- Direct intermolecular surface interactions leading to unusual assemblies in the gas and solute phase.
- Solvent structuring at their surfaces - especially in the case of water.

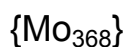
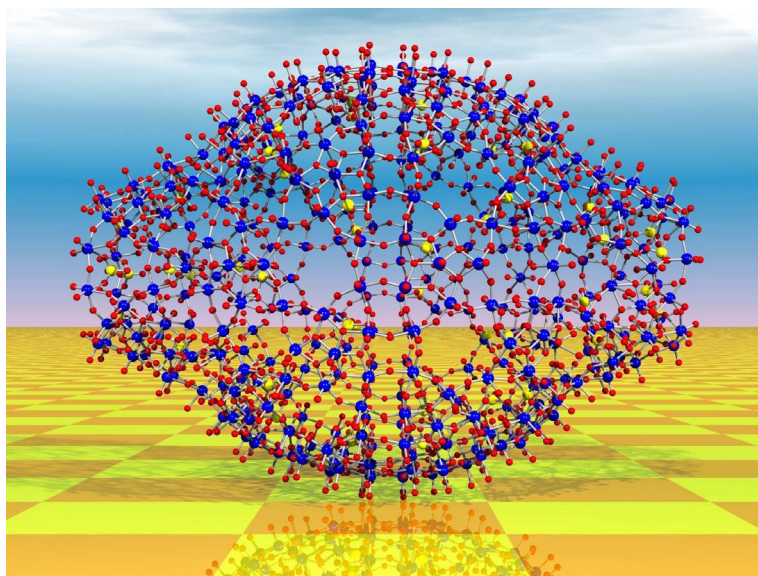
- Placing different groups - including the far-reaching multiphilic species - at different positions, which can lead to unusual multifunctional landscapes/surfaces and unprecedented surface structures (see Figures as well as the first and the second last cited paper) and allosteric effects.
 - Reactions/interactions at external as well as internal surface positions of both the covalent and non-covalent type. This even allows the fixation/encapsulation of a cluster inside the cavity based on non-covalent interactions leading to a new type of supramolecular compound.
 - Cross-linking in a solid state reaction at room temperature in case of the abundance of highly reactive surface functionalities (like $\text{Fe}(\text{H}_2\text{O})^{3+}$).
 - Metal-oxide based nucleation under confined conditions, starting with covalent linking from internal surface sites, as in case of molecular wheel cavities (last paper).
-
- **"Synergetic activation of "silent receptor" sites leading to a new type of inclusion complex: integration of a 64-membered ring comprising K^+ and SO_4^{2-} ions into a molybdenum oxide-based nanoobject"**, Chem. Comm., 2000-2001 (2003)
 - **"Paramagnetic Keplerate "Necklaces" Synthesized by a Novel Room-Temperature Solid-State Reaction: Controlled Linking of Metal-Oxide-Based Nanoparticles"**, Angew. Chem. Int. Ed. 41, 579-582 (2002)
 - **"'Molecular Symmetry Breakers' Generating Metal-Oxide-Based Nanoobject Fragments as Synthons for Complex Structures: $[\{\text{Mo}_{128}\text{Eu}_4\text{O}_{388}\text{H}_{10}(\text{H}_2\text{O})_{81}\}_2]^{20-}$, a Giant Cluster Dimer"**, Angew. Chem. Int. Ed. 41, 2805-2808 (2002)
 - **"Soccer-playing metal oxide giant spheres: a first step towards patterning structurally well defined nano-object collectives"**, Chem. Comm., 440-441 (2002)
 - **"Urea as 'deus ex machina' in giant molybdenum blue type cluster synthesis: an unusual hybrid compound with perspectives for related nano, supramolecular and extended structures"**, Chem. Comm., 2000-2002 (2002)
 - **"'Nanoobjects' by Self-Assembly Concomitant with Modifications under Alterable Boundary Conditions: Incorporation of Paramagnetic Metal Centers (Cu^{2+}) in Ring-Shaped Molybdenum-Oxide Based Clusters"**, Angew. Chem. Int. Ed. 40, 4034-4037 (2001)
 - **"On the option of generating novel type surfaces with multiphilic ligands within the cavity of a giant metal-oxide based wheel type cluster: chemical reactions with well-defined nanoobjects"**, Chem. Comm., 655-656 (2001)
 - **"Generation of cluster capsules (I_h) from decomposition products of a smaller cluster (Keggin - T_d) while surviving ones get encapsulated: species with core-shell topology formed by a fundamental symmetry-driven reaction"**, Chem. Comm., 657-658 (2001)
 - **"Linking Icosahedral, Strong Molecular Magnets $\{\text{Mo}^{\text{VI}}_{72}\text{Fe}^{\text{III}}_{30}\}$ to Layers - A Solid-State Reaction at Room Temperature"**, Angew. Chem. Int. Ed. Engl. 39, 1612-1614 (2000)
 - **"A New Type of Supramolecular Compound: Molybdenum-Oxide-Based Composites Consisting of Magnetic Nanocapsules with Encapsulated Keggin-Ion Electron Reservoirs Cross-Linked to a Two-Dimensional Network"**, Angew. Chem. Int. Ed. 39, 3413-3417 (2000)
 - **"Assembling nanosized ring-shaped synthons to an anionic layer structure based on the synergetically induced functional complementarity of their surface-sites: $\text{Na}_{21}[\text{Mo}^{\text{VI}}_{126}\text{Mo}^{\text{V}}_{28}\text{O}_{462}\text{H}_{14}(\text{H}_2\text{O})_{54}(\text{H}_2\text{PO}_2)_7] \cdot x \text{H}_2\text{O}$ ($x \approx 300$)"**, Chem. Comm., 1035-1036 (1999)

- **"Molecular growth from a Mo₁₇₆ to a Mo₂₄₈ cluster"**, Nature 397, 48-50 (1999)

Highlighted, e.g. in:

- D. A. Schiraldi, "An Unusual Inorganic 64-Membered Ring", "Heart Cut" (website of the American Chemical Society), 8.9.2003.
- G. R. Desiraju, "Chemistry beyond the molecule", Nature 2001, 412, 397-400.
- J. Uppenbrink, "A Soupçon of Phosphate", Science (Editors' Choice) 2000, 290, 411.
- A. Gerhard, "Molekulare Riesenräder verknüpft", Frankfurter Allgemeine Zeitung, 24. September 1997.

Dynamical Library Building Units Number-Increase Can Lead to Ever Larger Nanoscaled Assemblies: Symmetry Breaking at a Giant Cluster Surface



The nanocosmos as such, does not show the variety-limiting translational symmetry restriction of macroscopic crystalline materials but offers - in contrast to the "microcosmos" with its small molecules - the possibility that (several) larger arrays with local symmetries differing from the overall symmetry occur, a situation well known for spherical viruses and which increases the option for the generation of an extreme structural variety tremendously. Thus the appropriate building units must display a certain type of flexibility as prerequisite for linking, a condition well-fulfilled by molybdenum-oxide based fragments/aggregates under reducing conditions (i.e., those occurring in molybdenum blue solutions). These fragments abundant as potential ingredients of a "dynamic library", can, by a type of "split-and-link process", adapt their size and shape dependent on slight alterations of the relevant boundary conditions which can lead to the formation of a variety of unusual giant molybdenum-oxide based clusters. A unique example corresponds to the formation of a cluster with the size of hemoglobin (diameter approximately 6 nm), which contains 1880 non-hydrogen (368 metal) atoms. It is formed by the linking of 64 {Mo₁}-, 32 {Mo₂}-, and 40 {Mo(Mo₅)}-type units

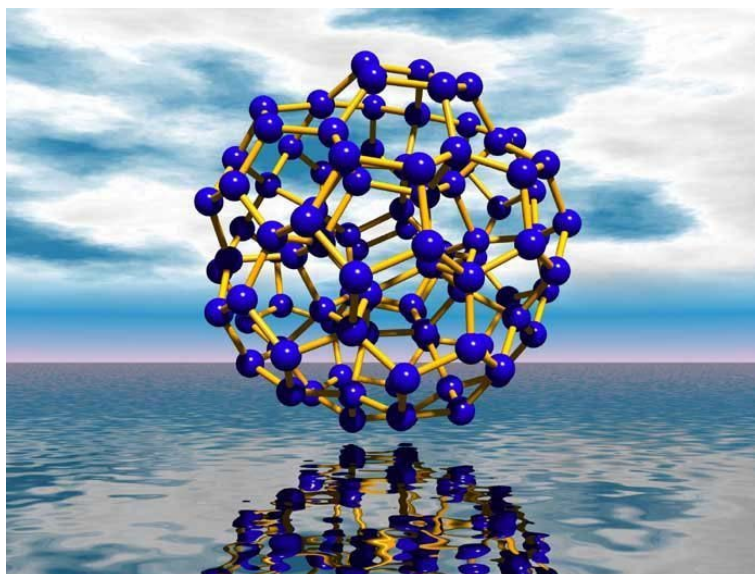
(exhibiting different stoichiometries) according to a remarkable symmetry-breaking process, which is nicely recognizable at the cluster surface (see Figure; Mo blue, O red, S yellow).

-
- **"On the complex hedgehog-shaped cluster species containing 368 Mo atoms: simple preparation method, new spectral details and information about the unique formation"**, Polyhedron 23, 2381-2385 (2004)
 - **"Inorganic Chemistry Goes Protein Size: A Mo₃₆₈ Nano-Hedgehog Initiating Nanochemistry by Symmetry Breaking"**, Angew. Chem. Int. Ed. 41, 1162-1167 (2002)

Highlighted, e.g. in:

- Encyclopaedia Britannica, 2004. Encyclopaedia Britannica Premium Service. "Mathematics and Physical Sciences". 6.11.2004 (<http://www.britannica.com/eb/article?tocId=91842>).
- R. Kurschat, "Ein Igel im Nanoformat: Molybdän-Cluster erreicht die Größe von Eiweißmolekülen", Neue Zürcher Zeitung, 15.5.2002.
- M. Sokolov, V. Fedin, "Record in Inorganic Chemistry", Nauka v Sibiri (Science in Siberia), Issue 2358-2359, June 2002.
- M. Gross, "Molybdates make a nano-hedgehog", Chemistry in Britain, 2002, 38, 16.
- P. Hergersberg, "Deutsche Chemiker bauten das größte Molekül", Die Welt, 23.5.2002.
- R. Kurschat, "Ein Igel im Nanoformat: Molybdän-Cluster erreicht die Größe von Eiweißmolekülen", Neue Zürcher Zeitung, 15.5.2002.
- P. Ball, "The blue lemon", Nature, materials update, 25.4.2002.
- D. Bradley, "Nano the Hedgehog", The Alchemist, News Research, 18.4.2002.
- "Winzige Riesenkugel", Die Zeit, 8.5.2002.
- S. Stinson, "Molybdenum blue puzzle may be solved", Chemical & Engineering News 3.6.1996.

Confined Water and the Mystery of the Liquid





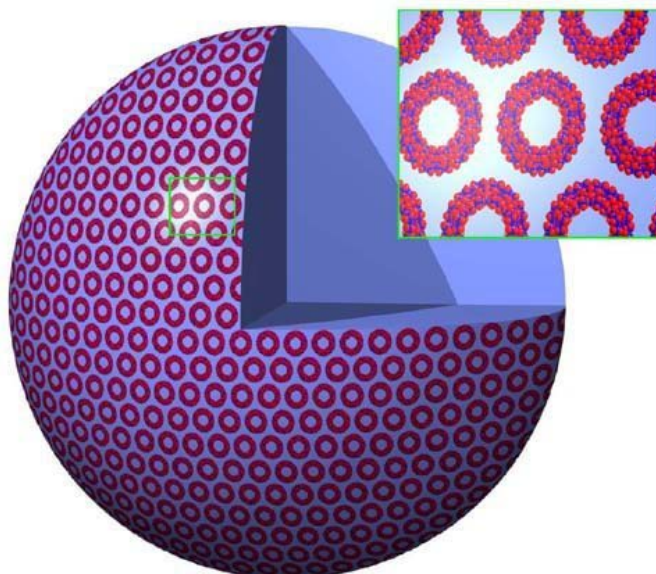
The properties and structure of "The Liquid Water" including its behaviour as a function of temperature and/or pressure as well as in the presence of (poly)electrolytes are yet not well understood. An important investigation, particularly for an understanding of several aspects of the role of water in biological processes, would be to study how moderately large assemblies of water molecules - say from 10 to 1000 - respond to their confinement in nanometer-sized cavities. (Note: In biological cells the water between biomolecules consists only of a rather small number of layers of molecules.) In the context of our work on "Encapsulation Chemistry" it is possible to influence encapsulated water-assembly structures on a wide range by the size, charge, internal surface, and encapsulated electrolytes as well as the capsule-hosts. The obtained information also provides general knowledge about the intrinsic properties of water molecules in general as well as about their potentiality to aggregate stepwise under confined conditions. The largest water cluster obtained consists of 100 H₂O molecules (Figure).

-
- **"Chameleon Water: Assemblies Confined in Nanocapsules"**, J. Mol. Liquids, 118,155-162 (2005)
 - **"Structure of a cavity-encapsulated nanodrop of water"**, Inorg. Chem. Comm. 6, 52-53 (2003)
 - **"Drawing Small Cations into Highly Charged Porous Nanocontainers Reveals "Water" Assembly and Related Interaction Problems"**, Angew. Chem. Int. Ed. 42, 2085-2090 (2003)

Highlighted, e.g. in:

- G. Zosimo-Landolfo, "À la découverte de l'eau", Biofutur 2003, Feb. Issue, p.17.
- R. Kurschat, "Wasser in Gefangenschaft - Winzige Käfige helfen bei der Analyse von Molekülclustern", Frankfurter Allgemeine Zeitung, 3.11.2003.
- N. Izarova, V. Fedin, "Nanodrop of water in the giant spherical cluster", Nauka v Sibiri (Science in Siberia), Issue 2386, December 2002.

Unprecedented Vesicle Formed From Wheel-Shaped-Type Clusters Exhibiting Hydrophilic Surfaces: A New Solute State of Inorganic Ions



New type of vesicle

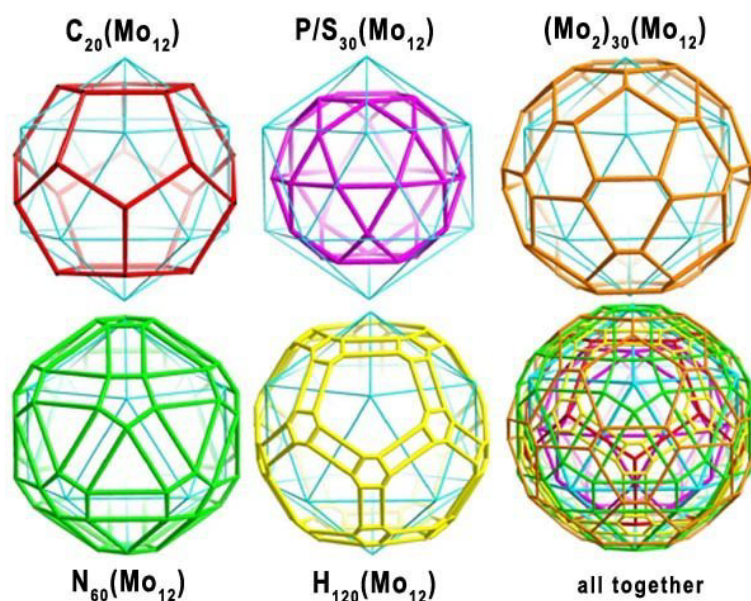
Special kinds of molecules abundant in solution can aggregate to different kinds of superstructured hierarchies: surfactants and membrane lipids can assemble into complex structures such as micelles, liposomes, or hollow vesicles due to their amphiphilic character. The wheel-shaped clusters, isolated from molybdenum blue solutions, with their hydrophilic surfaces and related high solubility, like the "classical" Mo_{154} , form in aqueous solution an unprecedented type of (hollow) superstructure/vesicle, where ca. 1200 molecular wheels form a sphere (80 nm diameter) with an encapsulated nanodrop of water (Figure). According to the rather large hydrophilic cluster surface, the interface water gets structured (proven by dielectric spectroscopy), which probably contributes to the formation of vesicles and may be described also by a new inorganic ion solute state. The high solubility prevented the isolation of crystals from Mo blue solutions for more than 200 years, since the first experiments were done by Scheele and Berzelius

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- **"Self-assembly in aqueous solution of wheel-shaped Mo_{154} oxide clusters into vesicles"**, Nature 426, 58 (2003)
 - **"Hierarchic patterning: architectures beyond 'giant molecular wheels'"** Chem. Comm., 1928-1929 (2001)

Highlighted, e.g. in:

- "Rounding up nanoclusters - nanotechnology", Materials Today 2004, Jan. Issue, p. 10.
- "Hohlkugel aus Riesenrädern", Spektrum der Wissenschaft 2004, Jan. Issue, p. 9.
- R. Kurschat, "Eine anorganische Haut für Wassertröpfchen", Neue Zürcher Zeitung, 19.11.2003.

Icosahedral Nanocapsules' Interpenetrating Platonic and Archimedean Solids: Chemistry and Aesthetics



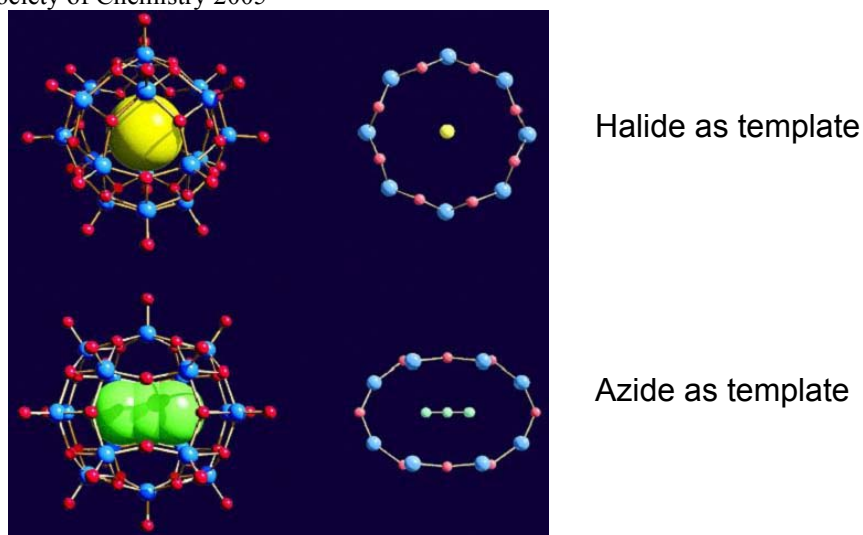
As the capsules of the type $\{\text{Pentagon}\}_{12}\{\text{Linker}\}_{30}$ have the highest possible (icosahedral) symmetry for molecules, a large number of sets of equivalent integrated as well as encapsulated atoms/species (like water molecules) are automatically generated, which span several more or less distorted Platonic and Archimedean solids. The architectural variety of such interpenetrating solids even fascinates mathematicians. The complex cluster system $[\{(\text{NH}_2)_3\text{C}^+\}_{20} + (\{\text{H}_2\text{O}\}_{20} \subset \{\text{H}_2\text{O}\}_{20} \subset \{\text{H}_2\text{O}\}_{60}) \subset \{(\text{Mo})\text{Mo}_5\text{O}_{21}(\text{H}_2\text{O})_6\}_{12} \{\text{Mo}_2\text{O}_4(\text{SO}_4/\text{H}_2\text{PO}_2)_2\}_{30}]^{32-}$ shows, e.g. the following solids: an icosahedron (blue), dodecahedron (red), icosidodecahedron (violet), truncated icosahedron (brown), rhombicosidodecahedron (green), and rhombitruncated icosidodecahedron (yellow) spanned by 12 Mo, 20 C, 30 S/P, 30 Mo_2 , 60 N, and 120 H, respectively (Figure). Surprisingly, the ratio of edges of the 30 rectangles of the $\{\text{H}_2\text{O}\}_{60}$ shell is very near to the value of the 'golden section' (i.e., ca. 1.6). In this sense the Platonic philosophy of beauty, truth and good can be referred to - if one also takes into account the importance of water for our, and all organisms' daily life in the context of the statements of Thales and Paracelsus.

-
- "The Beauty of Symmetry", Science (Perspectives) 300, 749-750 (2003)

Highlighted, e.g. in:

- R. Dagani, "Like a fullerene, but no carbon", Chem. & Eng. News 2003, 81, 13.
- T. Phillips, S. Brook, "Beyond Buckyballs", American Mathematical Society, July 2003 (referring to our publication on "The Beauty of Symmetry", Science 2003, 300, 749).

Templates Direct Fragment Linking Like Conductors



During the generation of giant polyoxometalate clusters template-directing processes are often involved. A nice text-book example refers to the controlled linking of $O=VO_4$ fragments. The templates are either added to the reaction mixture or are formed in it as "seedlings" (important aspect for a growth process; see last reference: "Unusual Stepwise Assembly and Molecular Growth [...]"); they regulate the mobility of the basic building blocks in solution and guide, like a conductor, the usually freely mobile fragments into a well-defined order. A comparison with the term "slaving principle" in the terminology of Hermann Haken's Synergetics is certainly worthwhile. In the present case, the finally formed system is of the host/guest type (see Fig.) where the host is complementary to the guest/template which is encapsulated.

Unusual Molecular Anion Cages: "The Taming of the Shrew"

The properties of ions in the solid state as well as in solution can in general only be evaluated in the presence of appropriate "perturbing" counterions being necessarily present due to the governing principle of electroneutrality. Therefore, it is very difficult to derive the properties of the free ions from spectroscopic data. However, this dilemma can be avoided by encapsulating anionic species as guests within a rigid host that is also negatively charged, for example a hollow isopolyvanadate, as mentioned above. This leads to relatively weak interactions, and hence, to rather large distances between the anions and the cluster shell. The resulting pseudomechanical fixation of the guests by the host offers the opportunity to have an almost isolated anion in a cryptand as object of scientific curiosity. The "corresponding counterions" in this case are located far away, outside the host-guest system, that is in the cationic lattice and have, therefore, no noticeable effect on the encapsulated anions.

-
- **"Formation of a Cluster Sheath around a Central Cluster by a 'Self-Organization Process': the Mixed Valence Polyoxovanadate $[V_{34}O_{82}]^{10-}$ ",** *Angew. Chem. Int. Ed. Engl.* 30, 588-590 (1991)
 - **"Induced molecule self-organization",** *Nature* 352, 115 (1991)
 - **"The Taming of the Shrew: Studying the Interaction of Ions with Ionic Carcerands as Molecular Containers",** *Naturwissenschaften* 80, 77-78 (1993)
 - **"Supramolecular Inorganic Chemistry: Small Guests in Small and Large Hosts",** *Angew. Chem. Int. Ed. Engl.* 34, 2328-2361 (1995) (review)
 - **"Polyoxometalates: Very Large Clusters - Nanoscale Magnets",** *Chemical Reviews* 98, 239-271 (1998)

- **"Unusual Stepwise Assembly and Molecular Growth: $[\text{H}_{14}\text{Mo}_{37}\text{O}_{112}]^{14-}$ and $[\text{H}_3\text{Mo}_{57}\text{V}_6(\text{NO})_6\text{O}_{189}(\text{H}_2\text{O})_{12}(\text{MoO})_6]^{21-}$ ", Chem. Eur. J. 4, 1000-1006 (1998)**

Highlighted, e.g. in:

- P. C. H. Mitchell, "Open and shut case for anions", Nature, 348 (1990), 15 (News and Views).
- M. T. Pope, "Anion guests in heteropolyanions?", Nature, 355 (1992), 27 (Scientific Correspondence).
- A. Dress, "Dirigenten komplexer Synthesen", Frankfurter Allgemeine Zeitung, 2. March 1994.