

# From Scheele and Berzelius to Müller

## Polyoxometalates (POMs) revisited and the “missing link” between the bottom up and top down approaches

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### Abstract

This review provides a survey of polyoxometalate chemistry with special emphasis on its history, and special attention to Souchay's and Müller's contributions. Polyoxometalates are early transition metal oxygen cluster anions. Considering their structures, sizes and properties, polyoxometalates are intermediate between small molecules and oxides. They have been known for more than two centuries, but due to the lack of appropriate analytical methods, the field remained for long one of the most confused in inorganic chemistry. It was Pierre Souchay (Faculty of Sciences in Paris/University Pierre et Marie Curie) who brought clarity in the field. He started a school which is still active today and has provided a major contribution to polyoxometalate chemistry. In the last fifteen years, polyoxometalate chemistry has expanded tremendously, following fundamental discoveries by Achim Müller at the University of Bielefeld. Achim Müller and his group have shown that aqueous solutions of molybdates allow the generation of a huge variety of combinatorially linkable units and, consequently, the formation of a large variety of clusters, among them amazing wheels and spheres. Such wheel-shaped clusters exist in “molybdenum blue” solutions which were known by Scheele and Berzelius and of which many generations of chemists failed to uncover the mystery. Wheels can be considered as nanostructured landscapes mimicking oxide surfaces and allowing reactions to occur at a variety of well-defined sites. Porous capsules are not less remarkable as their synthesis was deliberately planned and because they can be considered as artificial cells mimicking fundamental biological processes. Among the perspectives offered by these discoveries, encapsulation and generally speaking a new type of nanochemistry seem to be the most attractive.

### Keywords

**Polyoxometalates, molybdenum blue, artificial cells, encapsulation, nanostructured materials.**

### Résumé

**De Scheele et Berzelius à Müller : les polyoxométallates (POMs) revisités et le chaînon manquant entre les approches « bottom up » et « top down »**

Les polyoxométallates sont des clusters constitués de cations de début de série de transition et de haut degré d'oxydation, et de ligands oxo. De par leurs structures, leurs dimensions et leurs propriétés, ils sont intermédiaires entre les petites molécules et les oxydes. Ils sont connus depuis plus de deux siècles, mais en raison des difficultés d'analyse, ils ont longtemps constitué l'un des domaines les plus confus de la chimie inorganique. L'on doit à Pierre Souchay (Faculté des Sciences de Paris/Université Pierre et Marie Curie) et à ses élèves de l'avoir clarifié par une série d'études systématiques commencées vers 1940 et qui constituent une contribution majeure à la chimie des polyoxométallates. Depuis une quinzaine d'années, le domaine s'est prodigieusement développé sous l'impulsion d'Achim Müller à l'Université de Bielefeld. Achim Müller et son équipe ont montré que les solutions de molybdates permettent de générer une très grande variété de composants de construction. Des structures extraordinaires, notamment en forme de roues et de sphères, ont ainsi été obtenues. Les « roues » existent dans les « bleus de molybdène » connus de Scheele et de Berzelius et sur lesquels de nombreuses générations de chimistes s'étaient penchées sans parvenir à en percer le mystère. Ces roues peuvent être considérées comme des paysages nanostructurés simulant les surfaces d'oxydes et permettant d'effectuer des réactions en des sites bien définis. Les capsules ne sont pas moins remarquables car elles ont été obtenues de façon délibérée, et elles peuvent être considérées comme des cellules artificielles simulant des processus biologiques fondamentaux. Parmi les nombreuses perspectives ouvertes par ces découvertes, la chimie d'encapsulation semble être l'une des plus prometteuses.

### Mots-clés

**Polyoxométallates, bleu de molybdène, cellules artificielles, encapsulation, matériaux nanostructurés.**

Nearly half a century ago, Richard Feynman gave the first talk on nanotechnology, entitled “**There's plenty of room at the bottom**” [1], in which he stated: “*What I want to talk about is the problem of manipulating and controlling things on a small scale*”. At the end of his talk, he considered the pos-

sibility of direct manipulation of individual atoms as a powerful form of synthetic chemistry to construct larger molecules, which has been coined as the “bottom up” approach, in opposition to the “top down” approach consisting in the always more demanding miniaturization of devices.

Following the first approach, molecular chemists have perfected the art of producing molecules of ever increasing complexity using sophisticated multistep or even better one-pot syntheses, starting from molecular bricks and employing self-assembling rules and/or biomimetic processes. At the other extreme, following the “top down” approach, engineers of microelectronics have succeeded in fabricating the remarkable integrated circuits that control the world’s most powerful miniaturized computers. In between, there is a no man’s land, an uncharted world, coined “nanoworld”, in the size domain going from say a few nm to several 100 nm, which can not be easily reached by either molecular wires-related “covalent” chemists or three-dimensional matter “microlithograph” experts.

There are many examples where materials see a drastic change in their physical properties, from discrete to extended, for a certain critical size. This critical size concept has been expanded and may strongly differ depending on the property which is being studied. The latter may be physical, e.g. the colour and its associated quantum size effect [2], but also chemical, e.g. the catalytic hydrogenolysis of saturated hydrocarbons, and the associated ensemble of atoms required at the catalyst surface to promote this reaction [3], or simply geometrical (as size-dependent property), e.g. pores taken as molecular nanoreactors and as a way to control the molecular traffic in mesoporous materials, such as MCM-41 [4].

Much effort has thus been devoted to the determination of these critical sizes, which often lie in the nanometer range, and also to the corresponding nuclearity. Recent years have witnessed a formidable burst of research to unravel the mysteries and laws which control the construction of the nanoworld and its fascinating and yet often unknown properties.

It is precisely in this context that we are witnessing the remarkable progress made in the field of early transition metal oxygen cluster anions (PolyOxoMetalates or POMs) (voir *encadré*) [5]. We believe that the latter can be considered as the “missing link” between the bottom up and top down approaches to the expanding chemical nanoworld. Here the emphasis is to use concepts of self-assembly, based on both covalent and non-covalent interactions, host-guest chemistry, structural templates and bio-inspired processes.

As discussed below, POMs may also be regarded as a missing link between chemistry and several areas, notably discrete mathematics (e.g. symmetry and related tiling problems), physics (e.g. size-dependent phenomena), materials science (e.g. elaboration of nano-objects), biology (e.g. modelling

transmembrane ion transport, etc.), and aesthetics and architecture (e.g. simplicity and beauty of complex geometrical forms), in moving from the nano- to the macroscopic world.

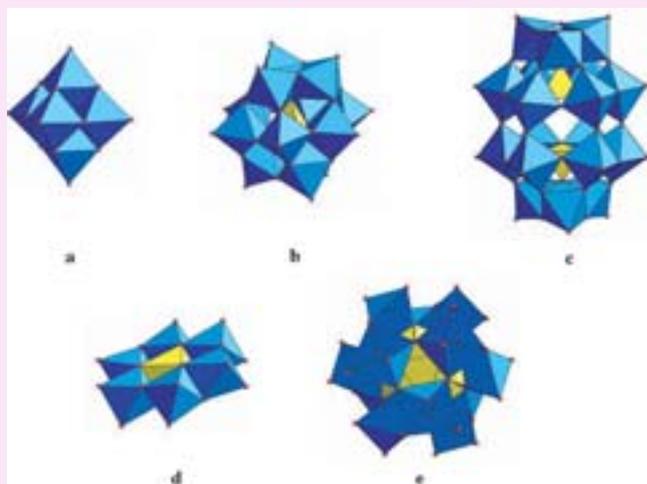
We present first a brief historical perspective of POM chemistry with emphasis on the French contribution and in the subsequent parts, we highlight the fantastic development of the field in Bielefeld during the last fifteen years: the discovery of giant polyoxomolybdates (wheels and spheres) by Müller and his co-workers is explained and the new options for chemistry offered by these nano-objects are discussed hereafter [5g]. Then, applications referring to materials, and conclusions and perspectives are outlined. For colleagues, not expert in the field, who are interested in basic POM chemistry, we refer to the review of Pope and Müller *Polyoxometalate Chemistry: An Old Field with New Dimensions in Several Disciplines* [5b].

## Classical POM chemistry: basic principles and the French contribution

POMs are a class of inorganic compounds that is unmatched not only in terms of molecular and electronic structural versatility, but also regarding reactivity and relevance to analytical chemistry, catalysis, biology, medicine, geochemistry, materials science and topology. The field is even getting more and more important from year to year. It is not by chance that some of the most famous chemists, e.g. Scheele (1742-1786), Berzelius (1779-1848), Werner (1866-1919) and Pauling (1901-1994), were interested in this field. Several French chemists have much contributed to the early development of POM chemistry but nevertheless, the most important contribution of French chemistry to the field was that of Souhay from 1940 to his death in 1974.

The first report of what we refer now to a POM dates back to Berzelius (1826) [6a] who described the yellow precipitate that is produced when ammonium molybdate is added in excess to phosphoric acid and which is now known as  $(\text{NH}_4)_3[\text{PMo}_{12}\text{O}_{40}]_{\text{aq}}$ , with the co-called 12:1 composition (we will come back to the important early work of Swedish chemists about molybdates hereafter; Berzelius also made many other fundamental contributions to chemistry: in particular, it was him who coined the word catalysis [6b]). However it was not until the discovery of the tungstosilicic acids and their salts by Galissard de Marignac in 1864 that the analytical composition of the 12:1 heteropoly species was precisely determined [7].

### Some common POM structures in polyhedral representations



a) The  $[\text{M}_6\text{O}_{19}]^{n-}$  “Lindqvist” structure ( $O_h$  symmetry) is a compact arrangement of six edge-shared  $\text{MO}_6$  octahedra (known for  $\text{M} = \text{Mo}, \text{W}, \text{Nb}, \text{Ta}$ ). b) The  $\alpha\text{-}\{[\text{XO}_4]\text{M}_{12}\text{O}_{36}\}^{n-}$  “Keggin” structure ( $T_d$  symmetry) is composed of four  $\text{M}_3\text{O}_{13}$  groups of three edge-shared  $\text{MO}_6$  octahedra, linked by corner-sharing to each other and to the central  $\text{XO}_4$  tetrahedron ( $\text{M} = \text{Mo}, \text{W}$ ;  $\text{X}$  can be a non-metal, e.g.  $\text{P}^{\text{V}}$  and  $\text{Si}^{\text{IV}}$  or a metal, e.g.  $\text{Co}^{\text{III}}$  and  $\text{Cu}^{\text{I}}$ ). c) The  $\alpha\text{-}\{[\text{XO}_4]\text{M}_{18}\text{O}_{54}\}^{n-}$  “Dawson” structure (maximum symmetry  $D_{3h}$ ) is made by fusion of two  $\text{A-}\alpha\text{-}\text{XM}_9\text{O}_{34}$  “Keggin” fragments (known for  $\text{M} = \text{Mo}, \text{W}$ ;  $\text{X} = \text{P}, \text{As}, \text{S}$ ). d) The  $[\text{H}_x\text{X}(\text{XO}_6)\text{M}_6\text{O}_{18}]^{n-}$  “Anderson” structure ( $D_{3d}$  symmetry) is a planar arrangement of seven edge-shared octahedra (e.g.  $\text{X} = \text{I}, \text{M} = \text{Mo}, x = 0, n = 5$ ;  $\text{X} = \text{Cr}, \text{M} = \text{Mo}, x = 6, n = 3$ ). e) The  $[\text{XO}_{12}\text{M}_{12}\text{O}_{30}]^{n-}$  structure (maximum symmetry  $I_h$ ) may be viewed as a  $\text{XO}_{12}$  icosahedron surrounded by six equivalent  $\text{M}_2\text{O}_9$  groups of face-shared  $\text{MoO}_6$  octahedra, linked together by corner-sharing (known for  $\text{M} = \text{Mo}, \text{X} =$  tetravalent lanthanide and actinide cations).

The first attempt to understand the composition of heteropolyanions was made by Werner himself who tried to explain the structures of 12:1 species on the basis of his new ideas on coordination chemistry for which he was highly recognized [8]. This was expressed as a structural hypothesis by Miolati and Pizzighelli in 1908 [9] and further developed by Rosenheim who made a systematic study of heteropolyanions during the first 35 years of the 20<sup>th</sup> century [10]. In the Miolati-Rosenheim hypothesis, the 12-molybdophosphoric acid was viewed as deriving from the hypothetical acid  $H_7[PO_6]$  through the replacement of the oxygen atoms by  $Mo_2O_7$  groups.

The Miolati-Rosenheim structural hypothesis, which largely contributed to shed light on a field which had been much confused until then because of the lack of appropriate analytical methods, prevailed until the late 1920s. Pauling then proposed that the principles mainly based on ionic radii and underlying the structures of ionic crystals should also apply to heteropolyanions [11]. The structures he elaborated turned out to be incorrect because he did not consider the possibility of edge-sharing between  $MO_6$  octahedra. A few years after Pauling's ideas, the crystal structure of  $H_3[PW_{12}O_{40}] \cdot 5H_2O$  was solved by Keggin [12a] (actual formulation as a hexahydrate of composition  $(H_5O_2)_3[PW_{12}O_{40}]$  [12b]).

To summarize: the evolution of the views on the composition and structure of heteropolyanions can be illustrated with the 12-tungstophosphoric acid which was written as  $H_7[P(W_2O_7)_6]$  (Miolati-Rosenheim), then as  $H_3[PO_4W_{12}O_{18}(OH)_3]$  (Pauling), and finally as  $H_3[P(W_3O_{10})_4]$  often written as  $H_3[PW_{12}O_{40}]$  (Keggin).

By the mid-20<sup>th</sup> century, hundreds of polyanions had been reported [10]. The chemical and physical properties of many of them had been described and there was some indication for their structures, but almost nothing was known about the reactions of formation, degradation and interconversion of these species in solution. It was Souchay who started the study of condensation reactions in solution [13]. A distinctive feature of his work is the extensive use of the polarography technique, invented by Heyrowsky in 1922. In addition to polarography and controlled potential reduction, Souchay also used various techniques, e.g. pH and solubility measurements, fused salt hydrate cryoscopy, spectrophotometry, magnetochemistry and ultracentrifugation. He wrote three books, one of which in collaboration with Lefebvre [14], and started a school which is still active today. It is noteworthy that three generations of chemists whose names are cited in references have been involved in POM chemistry in Paris since 1940.

Although Souchay's primary interest was in tungstates [13a], he also paid much attention to the reduction of  $Mo^{VI}$  in aqueous solutions [15a-c]. Interestingly, he also tried to understand the structure of "molybdenum blue" [15d]. Since 1961, the systematic study of the electrolytic reduction of polyanions has been the subject of several PhD works [16]. The exceptional ability of heteropolyanions to act as electron reservoirs was demonstrated by the preparation and characterization of numerous reduced derivatives, among which highly reduced species, e.g. the 32-electron reduced metatungstate anion [16c]. Reduced heteropolyanions with a number of electrons (multiple of six) were found to undergo intramolecular disproportionation driven by the localization of  $W^{IV}$  centers and the formation of three W-W bonds within an edge-sharing triad of  $WO_6$  octahedra. Interesting aspects of electron delocalization in mixed-valence polyanions were studied by optical and EPR spectroscopy [17].

Other significant contributions from Souchay and co-workers are outlined below:

- Investigation of the key parameters (pH, temperature, nature of the solvent, nature of the counter-ions, stereochemistry of the heteroatom) and making-out general schemes for the synthesis of polyoxometalates in solution [18].
- Clarification of isomerism in Keggin and Dawson type complexes [19].
- Chemistry of lacunary POMs [20]. In this context, the American chemist Finke wrote: "What is impressive is the ability of the French school to develop the chemistry of multiple metastable lacunary polyoxoanion species using primarily only polarography, IR, elemental analysis, and great intuitive insights plus careful experimental work as their main tools" [20e]. Lacunary POMs are known to form magnetic clusters with diverse nuclearities and original topologies [20f-g].
- Linking lacunary polytungstates to larger polyanions, e.g.  $[As_4W_{40}O_{140}]^{28-}$  and  $[P_8W_{48}O_{184}]^{40-}$  [21].
- Host-guest chemistry of inorganic cryptates, e.g.  $[Sb_9W_{21}O_{86}]^{19-}$  [22a] and  $[As_4W_{40}O_{140}]^{28-}$  [22b-d].
- Chemistry of fluoroisopolytungstates [23].

More recent developments include:

- The derivatization of POMs, notably through the incorporation of multiply bonded nitrogen ligands [24a] and the grafting of organosilyl and/or organophosphoryl groups on lacunary POMs [24b]. The functionalization of POMs is currently an active field of research with options for new applications in catalysis, medicine and nanosciences [24c].
- The emergence of polyoxothiometalate chemistry: the  $[Mo_2S_2(H_2O)_6]^{2+}$  precursor has been proved to be a "magic building block" for the design of cyclic structures which display striking host-guest chemistry [25].

Other aspects of POM chemistry, e.g. heterogeneous catalysis [26] and interaction of POMs with biomolecules, have also been explored. Antiviral activity of POMs was first reported in 1971 [27a]. Subsequent studies have shown their broad biological activity spectrum, especially that of  $[Sb_9W_{21}O_{86}]^{19-}$  (known as HPA-23) [27b]. The interface of POM chemistry with biology is still the subject of considerable interest [27c].

Since the early 70's, infrared and Raman spectroscopy have been extensively used, not only for fingerprinting but also, in favourable cases, for structural elucidation and the determination of force constants [28]; furthermore, multinuclear NMR studies have been developed over the last two decades [29]. Introduction of single-crystal X-ray diffraction techniques in the laboratory since the mid-seventies has allowed to solve the structures of many remarkable compounds, e.g.  $[NH_4(H_2O)_2Co_2As_4W_{40}O_{140}]^{23-}$  (figure 1a) [22c] and  $[H_7P_8W_{48}O_{184}]^{33-}$  (figure 1b) [20c], to name a few. Host-guest chemistry based on  $[As_4W_{40}O_{140}]^{28-}$  has been extensively investigated [22b]. Interestingly, it has been recently found that activation of the internal cavity shell through substitution of vanadium atoms of the  $\{\alpha-AsW_9\}$  units for tungsten centers provides new options for encapsulation chemistry [30]. The  $[P_8W_{48}O_{184}]^{40-}$  anion can be viewed as a condensed tetramer of metastable hexavacant derivative of the Dawson anion  $[P_2W_{18}O_{62}]^{6-}$ . It allows the study metal oxide-based nucleation processes in the cavity [31-32]. This led for instance to the  $Cu_{20}$  containing polyanion  $[Cu_{20}Cl(OH)_{24}(H_2O)_{12}(P_8W_{48}O_{184})]^{25-}$  [31], and also to  $\{V^{IV}(H_2O)_4(V^{V}_2O_5)_4(P_8W_{48}O_{184})\}^{24-}$  in which the cavity is capped by two  $\{V^{IV}_2V^{V}_4O_{12}(H_2O)_2\}^{4+}$  groups [32].

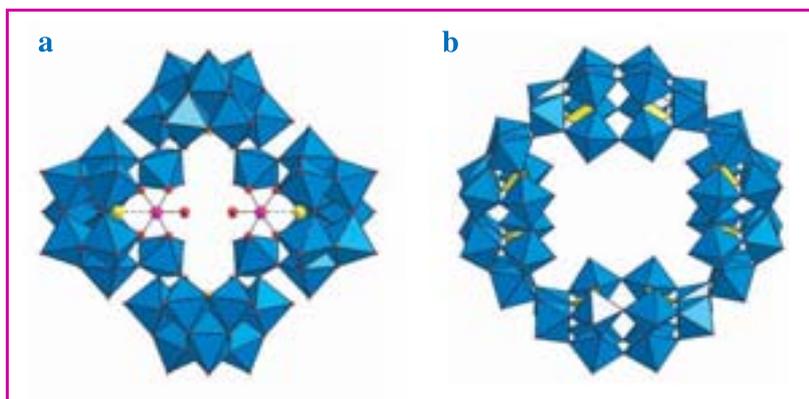


Figure 1 - a) The  $[\text{As}_4\text{W}_{40}\text{O}_{140}]^{28-}$  anion is made of four  $\{\alpha\text{-AsW}_9\}$  units linked by four additional tungsten atoms. It has a central cavity defined by eight oxygen atoms in a very distorted cubic geometry, surrounded by four smaller binding sites defined by four oxygen atoms and an arsenic atom in a square pyramidal geometry. Colour code:  $\text{WO}_6$  octahedra: blue, arsenic: yellow, cobalt: pink, oxygen: red [22c]. b) The  $[\text{P}_8\text{W}_{48}\text{O}_{184}]^{40-}$  anion can be viewed as a condensed tetramer of metastable hexavacant derivative of the Dawson anion  $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ . Colour code:  $\text{WO}_6$  octahedra: blue,  $\text{PO}_4$  tetrahedra: yellow [20c].

In retrospect, the work by Souchay and co-workers at the Université of Paris, along with that of a few other groups, notably in Georgetown University (Baker, Pope) have brought POMs into the realm of modern inorganic chemistry and drawn the attention of workers of various chemical areas to the great potential of these compounds.

## From wheels to nanocapsules: how it all began in Bielefeld

### Mystery of “molybdenum blue” and discovery of the Bielefeld giant wheel

During the last 15 years, POM chemistry has, following fundamental discoveries in Bielefeld, completely changed in nature and can be considered as the basis of a new type of nanochemistry and nanomaterials science [33]. The route to these emergent fields was stimulated by the combinatorial strategies that Nature employs to construct assemblies of complex molecules with specific forms and functions. Achim Müller's approach was full of imagination in the exploration of the versatile chemical behaviour of molybdates under reducing conditions by creating self-assembling systems in solution. This development has certainly been favoured by the existence of the Interdisciplinary Research Center (Zentrum für Interdisziplinäre Forschung, ZiF) at the University of Bielefeld where biologists, chemists, physicists, mathematicians and philosophers regularly meet and discuss.

The discovery of the Bielefeld giant wheel has its origin in the determination of Müller to unravel the mystery of the intense blue colour obtained by the reduction of acidified solutions of molybdate ( $\text{Mo}^{\text{VI}}$ ). Interestingly, such solutions exist in Nature: centuries ago the Native Americans observed the “blue waters”, solutions of “molybdenum blue” formed by partial oxidation of molybdenite  $\text{MoS}_2$  (leading to the mineral ilsemannite, with approximate formula  $\text{Mo}_3\text{O}_8 \cdot n\text{H}_2\text{O}$ ) near today's Idaho Springs and the Valley of the Ten Thousand Smokes. The “molybdenum blue” solution was first studied by the famous Swedish chemists Scheele and Berzelius. It was Scheele who described the first reproducible experiment related to molybdenum blue: “*Chemische Untersuchung über das Molybdänum oder Wasserbley*” (*Chemical studies on molybdenum or water lead*) [34a]. Scheele was already aware

that molybdenum blue was a reduced molybdenum oxide. However, it took almost forty years before Berzelius reported the first formula ( $\text{Mo}_5\text{O}_{14} \cdot n\text{H}_2\text{O}$ ) for the blue powder isolated from such solutions [6a].

Afterwards, generations of chemists were puzzled over the nature of molybdenum blue (for the complete historical view, see ref. [34b-c]). In his famous classical textbook, Sidgwick mentioned: “*This is a substance or group of substances about which there has been much discussion*” [34d]. The solution exhibits the Tyndall effect while the extent of light scattering increases with time. The existence of a time dependent growth process was first proven with SAXS (Small Angle X-ray Scattering) [35-36].

In the mid-1990s, Müller and co-workers were able to isolate a few single crystals from a Mo blue solution obtained with  $\text{NH}_2\text{OH}$  as reducing agent [37a]. The structure analysis revealed two important features: i) the anion was a giant wheel-shaped polyoxomolybdate, 4 nanometres

in diameter, made up of 154 molybdenum atoms embedded in a network of oxygen atoms and ii) the large surface area of the anion and the large number of  $\text{H}_2\text{O}$  ligands were responsible for the high solubility of the compound. This paper attracted considerable attention [38b] and was highlighted as “*Big wheel rolls back molecular frontier*” [38a]. It should be mentioned that the determination of the formula was a real challenge. After the first formula was published with an error limit for the negative charge (due to uncertainty on the number of protons), the Bielefeld group worked for many months to find the final nowadays accepted stoichiometry  $[\text{Mo}_{154}(\text{NO})_{14}\text{O}_{448}\text{H}_{14}(\text{H}_2\text{O})_{70}]^{28-} \equiv [\text{Mo}_{126}^{\text{VI}}\text{Mo}_{28}^{\text{V}}] \equiv \{\text{Mo}_{154}\}$  [36].

Subsequent work showed that the  $\{\text{Mo}_{154}\}$  cluster is the basic structural type of molybdenum blue compounds obtained under slightly different conditions [37b]. The crystallization problem was solved by using the salting out procedure of protein chemistry or working under very high concentrations [37c]. Using a range of analytical techniques, Müller and co-workers were finally able to show that all the crystalline precipitates, obtained by reduction of acidified molybdate solution with different reducing agents, contain discrete ring-shaped anions, especially  $[\text{Mo}_{154}\text{O}_{462}\text{H}_{14}(\text{H}_2\text{O})_{70}]^{14-}$  (derived from  $[\text{Mo}_{154}(\text{NO})_{14}\text{O}_{448}\text{H}_{14}(\text{H}_2\text{O})_{70}]^{28-}$  by replacing the 14  $\{\text{MoNO}\}^{3+}$  by  $\{\text{MoO}\}^{4+}$  groups) (figure 2) [36-37b]. This was highlighted as “*Molybdenum blue puzzle may be solved*” [38c]. Interestingly, the formula can also be written as  $[(\text{MoO}_3)_{154}\text{H}_{14}(\text{H}_2\text{O})_{70}]^{14-}$  [36], which corresponds to a reduced protonated hydrated molecular molybdenum trioxide, the end-product of the polycondensation process. Since then, wheels with 176 and 248 molybdenum atoms have also been synthesized [39].

The original NO-containing cluster [37a] is only historically interesting as it would never be obtained in a pure form whereas  $[(\text{MoO}_3)_{154}\text{H}_{14}(\text{H}_2\text{O})_{70}]^{14-}$  can now be obtained in a facile synthesis and has correspondingly been published in *Inorganic Synthesis* and a student textbook [40a-b].

### From giant wheels to giant spheres

The next challenge was to go from wheels to the spherical systems. The success of the Bielefeld group was based not

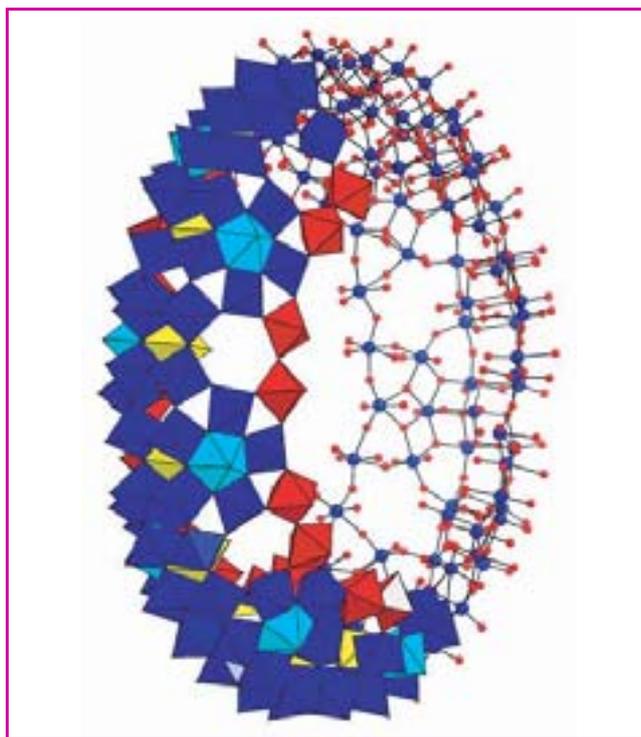
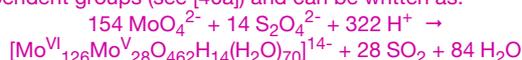


Figure 2 - The structure of the Bielefeld "wheel" contains 154 Mo atoms – half in polyhedral representation with different building units ( $\text{Mo}_8$  blue,  $\text{Mo}_2$  red,  $\text{Mo}_1$  yellow), and half in ball and stick representation (Mo blue, O red). Its synthesis has been tested by independent groups (see [40a]) and can be written as:

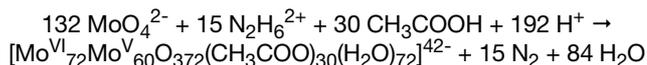


only on the expertise accumulated for the discovery of the molecular wheels but also and more remarkably on information available from other fields [41]: with the lessons drawn from architecture, virology and daily life, it became obvious that pentagonal building units were required to obtain spherical structures. Let us mention that in their *Biochemistry* textbook, D. and J.G. Voet underline that the virologists Klug and Caspar found inspiration in Fuller's geodesic dome to unravel the structure of spherical viruses [41f]. On the other hand until the discovery of its existence in alloys, penta-fold symmetry was not considered to be relevant to solid-state chemistry (note that tiling the plane with pentagons is not possible). Its discovery by Shechtman *et al.* in a metallic phase in 1984 [42] was considered as a paradigmatic shift.

It was known that the predominant species in aqueous solution at low pH values is a  $\{\text{Mo}_{36}\}$  type cluster which contains  $\{(\text{Mo})\text{Mo}_5\}$  units (one pentagonal  $\text{MoO}_7$  unit sharing edges with five  $\text{MoO}_6$  octahedra) [43]. Because the interaction of the pentagonal units with the "rest" of the cluster is not too strong as these are only connected *via* corners and on the other hand spherical systems are always preferably formed (a type of isoperimetric principle, *i.e.* minimal surface to volume ratio), spherical species were expected to form by adding linkers like  $\text{Mo}^{\text{V}}_2\text{O}_4^{2+}$ ,  $\text{Fe}^{3+}$  or  $\text{VO}^{2+}$  to the aqueous solution of the  $\{\text{Mo}_{36}\}$  cluster.

The resulting spherical systems can be described by the following general formulation:  $(\text{Pentagon})_{12}(\text{Linker})_{30}$  in agreement with the theorem of Euler. The first of these molybdenum superfullerenes – or "Keplerates" as they were called by Müller and now by others, too in reminiscence of the early

cosmos of Kepler – was made in 1998 according to the following reaction [40a]:



It is composed of 132 molybdenum atoms with an inner cluster shell of 60  $\text{Mo}^{\text{V}}$  atoms with icosahedral symmetry arranged like the  $\text{C}_{60}$  bucky ball [41c] and has 20 nanoscale pores and 20 channels providing access to the inside of the capsule (figure 3). The consequences of porosity will be presented hereafter. The compound is brown in contrary to the "blues" because the 60  $\text{Mo}^{\text{V}}$  centers are organized in 30  $\text{Mo}_2$  units by spin pairing (see figure 3).

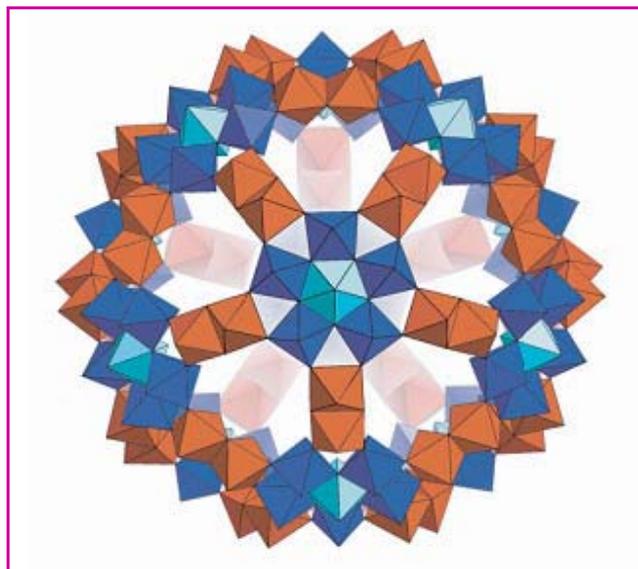
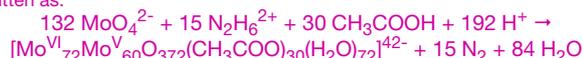


Figure 3 - Polyhedral representation of the porous capsule equivalent to an artificial cell: The first published Keplerate of the type  $\{\text{Mo}_{132}\}$ , an inorganic superfullerene built up by 12 pentagonal  $(\text{Mo})\text{Mo}_5$  based units (blue) and 30 different  $\text{Mo}^{\text{V}}_2$  based linkers (red). To emphasize the symmetry aspect of the capsule type, one can envision its structure with the following formula:  $\{[(\text{Mo}^{\text{VI}})\text{Mo}^{\text{V}}_5\text{O}_{21}(\text{H}_2\text{O})_6]_{12}(\text{Mo}_2\text{O}_4(\text{ligand}))_{30}\}^{n-}$ . The synthesis of the  $\{\text{Mo}_{132}\}$  capsule has been tested by independent groups (see [40a]) and can be written as:



Interestingly, the wheel and ball type structures can be written in the same way, *i.e.*  $\{\text{Pentagon}\}_n = \{(\text{Mo})\text{Mo}_5\text{Mo}'_5\}_n$  ( $n = 12$ : spherical systems;  $n = 14, 16$ : wheel type systems). The difference refers to the fact that whereas all  $\text{MoO}_6$  and  $\text{Mo}'\text{O}_6$  type octahedra are placed in the spherical systems in agreement with  $\text{C}_5$  symmetry, this is not the case for the wheels, where one  $\text{Mo}'\text{O}_6$  octahedron is displaced, which lowers the overall symmetry (for details see figures 3 and 4 in [44]). This was expressed in the following way: "Pythagorean Harmony in the World of Metal Oxygen Clusters of the  $\{\text{Mo}_{11}\}$  Type: Giant Wheels and Spheres both Based on a Pentagonal Type Unit" [44]. This formulation is based on the fact that the pentagon/fivestar was considered by the Pythagoreans as their secret symbol.

### Why molybdenum appears unique

Aqueous solutions of molybdates are unique in the sense that they allow the possibility of generation of a huge variety

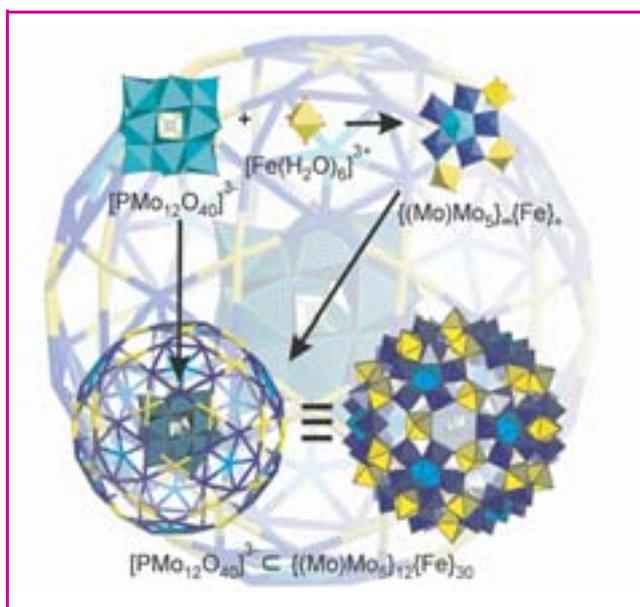


Figure 4 - Reaction scheme of Keggin anions (top left, polyhedral representation) with  $\text{Fe}^{\text{III}}$  ions.

Fragments of the type  $\{(\text{Mo})\text{Mo}_5\}_m\{\text{Fe}\}_n$  are generated which function as building blocks (top right, polyhedral representation) in the formation of  $\{(\text{Mo})\text{Mo}_5\}_{12}\{\text{Fe}\}_{30}$  type cages (bottom left: wireframe representation of the capsule (Mo atoms in blue and Fe in yellow); bottom right: polyhedral representation), where the remaining non-decomposed Keggin anions are encapsulated. The supramolecular species thus obtained possess the core-shell topology noted: guest  $\subset$  (pentagon) $_{12}$ (linker) $_{30}$ , i.e.  $\{\text{PMo}_{12}\text{O}_{40}\} \subset \{(\text{Mo})\text{Mo}_5\}_{12}\{\text{Fe}\}_{30}$  (colour code MoO $_{6/7}$  polyhedra: blue/turquoise, FeO $_6$  octahedra: yellow). The background highlights the host-guest composite obtained [47a].

of combinatorially linkable units as disposition [45, 46a]. It was found that a large variety of clusters and solid-state structures can be obtained by self-assembly processes in aqueous acidic solution in a controllable and tunable way under various but well-defined conditions. Protonation is a condition for growth and the size of the cluster is correspondingly controlled by the pH. This chemistry is unique and appears only possible for molybdenum. As an example, the reduction of a solution of tungstate(VI) leads to the formation of W-W bonds and therefore not to the appearance of electron density on the surface of the growing cluster, a condition for protonation and therefore growth [46a].

A nice illustration of the enormous flexibility of the molybdate system is demonstrated by the reaction of Keggin anions  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  with iron(III) ions. The Keggin ions decompose while their fragments form with the Fe(III) ions a giant icosahedral cluster with non-decomposed Keggin anions encapsulated. The Keggin anions have the right size to get encapsulated inside the cluster shell (figure 4) [47]. It appears that the more symmetrical icosahedral cluster wins over the less symmetrical Keggin ion to form a supramolecular structure.

In addition to wheels and capsules, the Bielefeld team prepared a huge cluster called “nano-hedgehog” because of its shape and also because it has an outer layer of oxygen atoms pointing outwards (figure 5). It contains 368 molybdenum atoms and has actually the size of a protein [47]. It has an internal cavity 2.5 nanometres wide and 4 nanometres long which encapsulates about 400 water molecules. The electron-rich cluster is deep blue in colour, due to delocalized electrons.

A comprehensive review about the synthetic and structural aspects of Müller’s work was published recently by Cronin [48].

## Specific interactions of molecular wheels and spheres with their environments: “Bringing inorganic chemistry to life” [33]

Molybdenum oxide based clusters are unique in that they not only form a wide variety of fascinating structures which can be obtained in crystalline solids in facile high-yield syntheses, but most important, they are stable, especially under exclusion of oxygen, flexible macromolecules which are highly soluble in water where they maintain their structure and functionality so that chemical reactions can be performed at specific sites.

In what follows, we distinguish spheres/capsules from wheels, which both show, besides functionality-dependent chemistry, shape-characteristic properties: giant wheels can be considered as nanostructured landscapes mimicking oxide surfaces and allowing reactions to occur at a variety of well-defined sites while porous capsules can be considered as artificial cells mimicking biological processes.

### Porous capsule-type clusters: nanochemistry under confined conditions

Molecular dimensioned holes are responsible for some useful properties of natural as well as synthetic materials, as they can serve as filters or trap molecules with well-defined shapes. Although a large number of porous materials exist as extended structures, there was, before Müller’s work, nearly nothing known about related structurally well-defined and tunable molecular nanoporous discrete species.

Spherical nanocapsules of the type  $\{(\text{Mo}^{\text{VI}})\text{Mo}^{\text{VI}}_5\text{O}_{21}(\text{H}_2\text{O})_6\}_{12}\{\text{Mo}_2\text{O}_4(\text{ligand})\}_{30}$  ( $\equiv\{\text{Mo}_{132}\}$ ) allow cutting-edge research relevant to different disciplines, like **chemistry** (e.g. modelling passive ion transport through membranes), **materials science** (e.g. nanoscale ion chromatography) and **physics** (e.g. confined matter properties). This is based on their unique features (figure 6) [49-50]:

- they have 20  $\{\text{Mo}_9\text{O}_9\}$  pores and a cavity connected to the outside via 20 channels,
- they behave as a semi-permeable inorganic membrane open for  $\text{H}_2\text{O}$  and small cations,

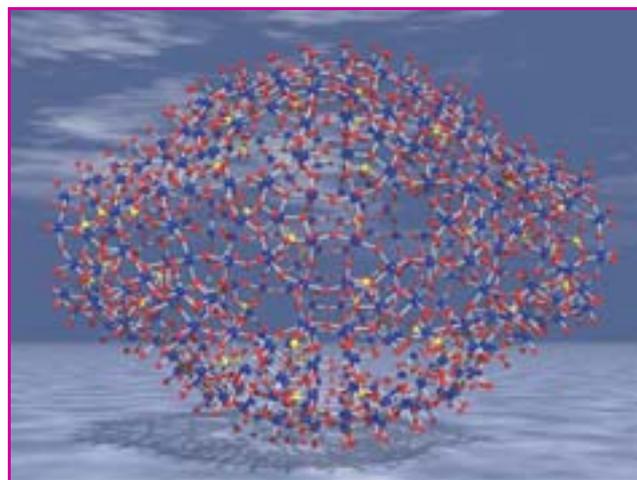


Figure 5 - Representation of the  $\{\text{Mo}_{368}\}$  type nanostructure called “nano-hedgehog” (the Mo atoms are blue, the O red, and the S yellow): “Inorganic Chemistry Goes Protein Size: A  $\text{Mo}_{368}$  Nano-Hedgehog Initiating Nanochemistry” (title of paper [46]).

- the 20  $\{\text{Mo}_9\text{O}_9\}$  pores of the capsule have crown-ether-like function and can be opened and closed with noncovalently bonded guests,
- the overall charge and the internal surface can be tuned by changing the ligands,
- they are quite stable both in aqueous and non-aqueous solvents in absence of oxygen.

#### • Cation traffic from the surface to the pores and channels

Capsules prove to be busy areas controlling molecular (especially cation) traffic in both directions through the channels. The following eight basic processes have been identified [51]: i) “wandering at the outer interface”, ii) “sticking at the outer interface”, iii) “recognition by pores”, iv) “recognition by channels”, v) “complexation at the inner interface”, vi) “encapsulation through clathrate formation”, vii) “recognition by water structure”, and viii) “breakdown of water structures”. More specifically, the traffic is governed by the concentration gradient (better electrochemical; see below) for the solvated cation dependent on the size of the cation and the lability of the water molecules in its hydration shell, the size of the pores, and the overall charge of the capsules.

#### **Nanoscale ion chromatography: traps for cations**

The interreaction of the negatively charged capsules with different cations in aqueous solution leads to a variety of architectures at the pores as well as in the channels or in the cavity. Different cations have distinct binding modes according to their size, shape, charge and hydration state, which results in well-defined cations separation, just as in the case of a “nanoscale ion chromatograph” (figure 7) [50]. (See highlight: “Traps for cations” which also refers to the behaviour of the  $[\text{As}_4\text{W}_{40}\text{O}_{140}]^{28-}$  anion [50b]).

#### **Traffic control through pore opening and closing**

When several types of cations are present, the highly charged ones, like  $\text{Pr}^{3+}$ , are preferably taken up thus stimulating the counter transport, *i.e.* the parallel release of  $\text{NH}_4^+$  by the capsule. Eventually this opens the route to a new type of coordination chemistry [52]. It was expected that more  $\text{Pr}^{3+}$  ions would be taken up under higher concentrations. However the formal “electrochemical gradient” across the channels approaches zero with sufficient uptake of  $\text{Pr}^{3+}$  so that the hydrated cations  $[\text{Pr}(\text{H}_2\text{O})_n]^{3+}$  that fail to make their way into the capsule find themselves “stuck” above the pores [53]. The traffic is hence regulated by a kind of “negative feedback” mechanism (figure 8). This was nicely described in a highlight: “Molecular guests stay at the gates” [53b].

Non-covalent pore-guest interactions with protonated bases are reversible so that the pores are not permanently closed in solution. For example, reaction of  $\text{Ca}^{2+}$  with a sulfate-based capsule – where the 20 pores are closed by protonated urea – allows the isolation of a new capsule where  $\text{Ca}^{2+}$  is taken up and where the pores are again closed with protonated urea. This process resembles the functioning of gated calcium channels in cell membranes [54a].

#### **Modelling passive ion transport through membranes**

The factors that determine trans-membrane cation transport, the influence of the environment and, in particular, the role of water as vehicle, can be addressed by NMR spectroscopy.

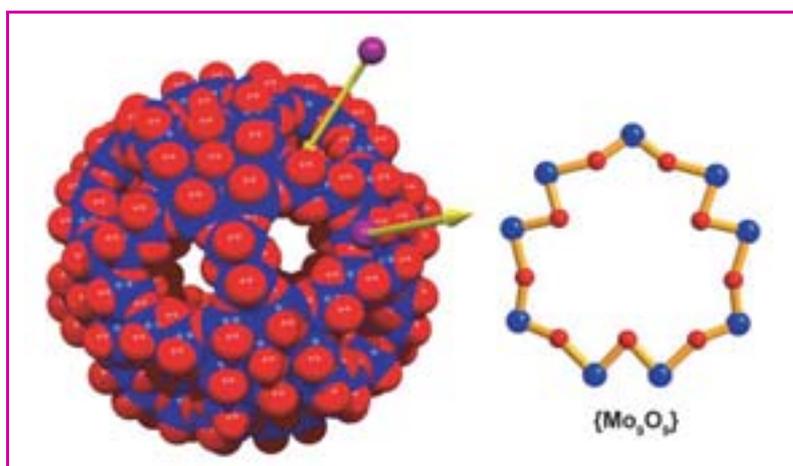


Figure 6 - Space-filling representation of the porous capsule equivalent to an artificial cell (left) emphasizing uptake and release of cations via the 20  $\{\text{Mo}_9\text{O}_9\}$  pores of the capsule (Mo atoms are blue, O red, and mobile cations lilac) [54b]. One of the pores (right) with crown-ether function is shown in ball-and-stick representation.

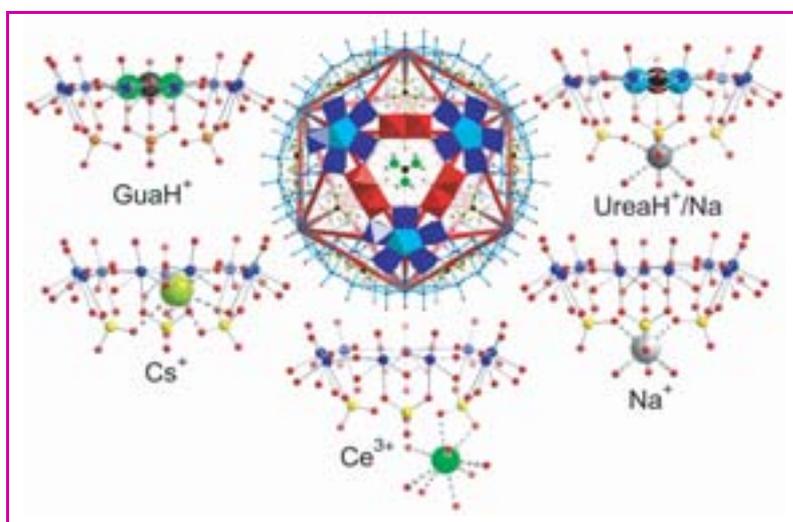


Figure 7 - Representation of the nanoscale ion chromatograph.

The middle top part represents the entrance of a  $\{\text{Mo}_9\text{O}_9\}$  pore, located on one of the 20 faces of the icosahedron spanned by 12  $\{(\text{Mo})\text{Mo}_5\}$  groups (pore shown in polyhedral representation emphasizing the 3  $\text{Mo}_2$  linkers and 3 pentagons, with a guanidinium guest). Different cations are held specifically at different positions of the pore and its adjoining channel, leading to the inside of the capsule of the type  $\{[(\text{Mo})\text{Mo}_5\text{O}_{21}(\text{H}_2\text{O})_6]_{12}(\text{Mo}_2\text{O}_4(\text{ligand}))_{30}\}$  (Mo atoms are blue, O red, S yellow, P/S brown, with respective substrates/cations in different colours) [50a].

copy. In this context,  $^7\text{Li}$  NMR studies of  $\text{Li}^+$  uptake/release processes by the sulfate-based  $\{\text{Mo}_{132}\}$  capsule in  $\text{DMSO}-d_6$  containing a small amount of water has revealed unprecedented features. Most importantly there is an equilibrium between  $\text{Li}^+$  uptake and release at room temperature, as shown by  $^7\text{Li}$ -EXSY NMR measurements [54b, 55a]. The situation has been compared with the equilibrium situation in the  $\text{K}^+$  leak channels which are ubiquitous in eukaryotic cells [56]. A similar situation also occurs with the  $\text{Na}^+$  capsule system [54b]. This is relevant to the  $\text{Li}^+/\text{Na}^+$  counter transport, which is of interest for hypertension research and plays a key role in the treatment of neuro-psychiatric disorders like manic depression [55b].

#### • Chemistry under confined conditions

##### **Coordination chemistry**

The  $\text{Pr}^{3+}$  cations encapsulated in the sulfate-based  $\{\text{Mo}_{132}\}$  capsule are found at two different sites and have two

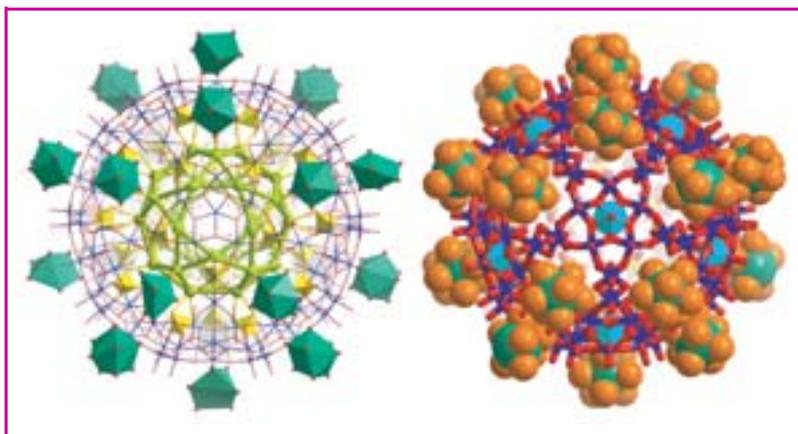


Figure 8 - Structure of the porous anionic capsule of the type  $\{(Mo)Mo_5\}_{12}\{Mo_2(SO_4)\}_{30}$  (left) emphasizing the outer hydrated  $Pr^{3+}$  ions (dark green polyhedra) as well as the inner  $Pr^{3+}$  ions forming an under-occupied icosidodecahedron (light green). The metal oxide skeleton of the capsule (illustrated in wire-frame model with Mo atoms in blue and O in red) and  $SO_4^{2-}$  ions (yellow tetrahedra) are shown additionally. Space-filling representation of the outer, hydrated  $Pr^{3+}$  ions with the metal oxide capsule skeleton (right) shown as a wire-frame model (same colour code as on the left) with the central pentagonal bipyramids of the pentagonal units shown in polyhedral representation (light blue) [53a].

different coordination shells corresponding to a coordination chemistry under confined conditions. The coordination polyhedra – a distorted cube and a distorted mono-capped octahedron – are formed by sulfate and  $H_2O$  ligands which belong to different encapsulated water shells, acting formally as polydentate ligands [52]. Interestingly, the underoccupied  $Pr^{3+}$  positions span two polyhedra, a dodecahedron and an icosidodecahedron.

### Fascinating water structures

In relation with the 2005 Year of Physics, a special issue of the *Journal of the CNRS* has been devoted to the ten mysteries of physics, listing water as number one. As a matter of fact, its structure and properties are still far from being understood. This statement could well apply to the fields of chemistry and biology as well, so overwhelming is the role of water in chemical and life processes [57].

One aspect of particular relevance refers to the problem of the structure of “water under confined conditions”. Closing the pores leads, in the case of the  $\{Mo_{132}\}$  cluster containing hypophosphite and sulfate ligands, to the reorganization of internal  $H_2O$  molecules into a giant and structurally well-defined  $(H_2O)_{100}$  cluster. The latter can be formally arranged in three concentric shells (two  $(H_2O)_{20}$  dodecahedra and one  $(H_2O)_{60}$  rhombicosidodecahedron); see [49, 58-59] and figure 9. This process of endohedral hierarchic arrangement of water molecules after pore closing is formally comparable to the response of the cell to a stimulus of its surface.

This is only one example: the water assembly can be modified by changing, e.g. the container size (in smaller  $\{Mo_{102}\}$  capsules, a  $(H_2O)_{40}$  cluster can be generated (figure 9)), the functionalities of the internal capsule shell and by encapsulating cations [59c].

### Nucleation processes

Another fascinating point refers to the possibility of performing different types of reactions inside the cavities at well-defined sites. For instance, the acetate-based  $\{Mo_{132}\}$  capsule proves to react with phosphate and molybdate (formed through partial decomposition of the capsule) in aqueous

solution leading to the formation of new P-O-Mo bonds at low pH [50a]. This phenomenon is reminiscent of the process of formation of the  $[PMo_{12}O_{40}]^{3-}$  Keggin anion (see previously).

### Wheel-type clusters: nanostructured landscapes with well-defined reaction sites

Wheel-type clusters possess the following characteristic properties:

- they exhibit a nanosized “torus” cavity,
  - they have an extended hydrophilic inner and outer surface,
  - they show  $n$  tetrahedral  $\{O_4\}$  and  $\{Mo_6O_6\}$  type ring receptors having nucleophilic properties ( $n = 14$  or 16),
  - it is possible to generate discrete structural defects at the inner surface of the wheels,
  - $H_2O$  ligands can be replaced by other ligands.
- These structural functionalities allow reactions to take place at a variety of well-defined sites. Furthermore, the chemistry within the wheels depends significantly on their size [39, 60-62].

### • $\{Mo_{154}\}$ wheel: unprecedented (surface) reactions

The replacement of water coordinated to the molybdenum centres of the  $\{Mo_{154}\}$  wheel by ambivalent and/or multivalent

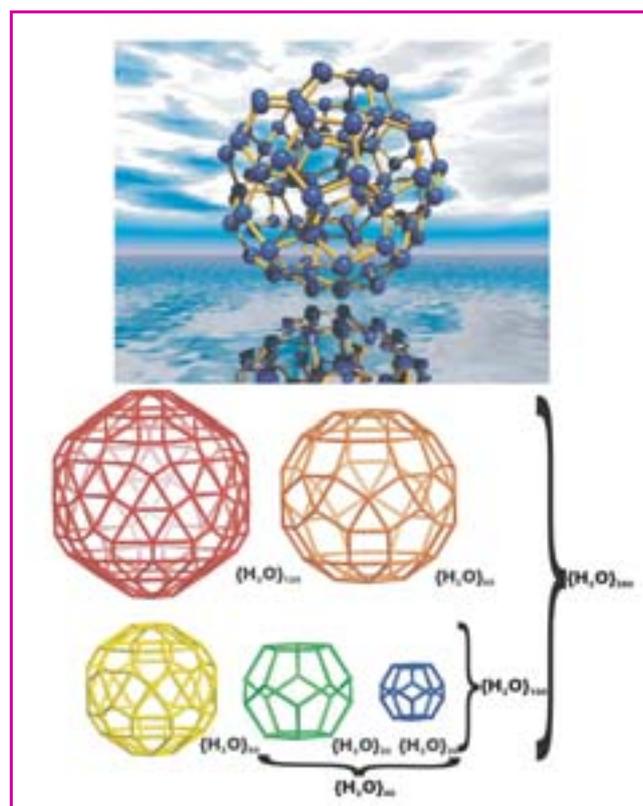


Figure 9 - From confined water to the aesthetics of Platonic and Archimedean solids.

Remarkable hierarchization of  $\{H_2O\}_n$  shells: the  $\{H_2O\}_{280}$  assembly obtained from molecular dynamics calculations for liquid water by M. Chaplin (containing all five properly connected shells/polytopes shown; for related literature see [59c]),  $\{H_2O\}_{100}$  (shown separately at the top) occurring in the capsule of  $\{[(NH_2)_3C^+]_{20}\} - \{(Mo)Mo_5O_2(H_2O)_6\}_{12}\{Mo_2O_4(SO_4)\}_{10}\{Mo_2O_4(H_2PO_2)\}_{20}\}^{32-}$  in the form of three shells/polytopes (in red, green and blue) properly connected with hydrogen bonds (shown at the bottom), and  $\{H_2O\}_{40}$  found in the  $\{(Mo)Mo_5\}_{12}\{Mo_6O_6\}_{30}$  type cluster cavity built up by the two  $\{H_2O\}_{20}$  dodecahedra (shown in green and blue). The fascinating aspect is that the  $\{H_2O\}_{100}$  assembly represents the center of  $\{H_2O\}_{280}$  (for details see [49, 58-59]).

ligands, for example the amino acid cystine, creates hydrophobic and hydrophilic surroundings on the inner wall of the cluster (*figure 10*) [60].

Paramagnetic metal centres like  $\text{Cu}^{2+}$  ions can be incorporated into tetrahedra defined by four O atoms and having the appropriate size. This may pave the way to the formation of nano-objects with unique magnetic and possibly catalytic properties [62a], because the active sites are embedded in an electron-rich environment.

The molecular wheels offer nucleophilic  $\{\text{Mo}_6\text{O}_6\}$  sites which act as (weak) receptors for cations, for example protonated urea guests [62b].

#### • $\{\text{Mo}_{176}\}$ wheel: unprecedented chemistry inside its cavity

The hexadecameric  $\{\text{Mo}_{176}\}$ -type cluster shows a manifold of (16 + 16) non-equivalent weak/silent receptor sites for cations as well as anions and allows, for example, the formation of a novel host-guest system by simultaneous integration of 16  $\text{K}^+$  and 16  $\text{SO}_4^{2-}$  ions and leading to an unusual 64-membered ring [61]. The related paper was entitled: “*Synergetic activation of “silent receptor” sites leading to a new type of inclusion complex: integration of a 64-membered ring comprising  $\text{K}^+$  and  $\text{SO}_4^{2-}$  ions into a molybdenum oxide-based nano-object*”. The cations are connected with the nucleophilic  $\text{Mo}_6\text{O}_6$  pores and the  $\text{SO}_4^{2-}$  ion has the same position as the  $\text{CuO}_4$  unit mentioned above. The smaller tetradecameric wheels would not be able to stabilize a  $\{\text{KSO}_4\}_{14}$  ring because of repulsive forces within the smaller ring.

The remarkable “addition” of two neutral  $\{\text{Mo}_{36}\}$ -type “hub-caps” to one  $\{\text{Mo}_{176}\}$  wheel leads to the formation of a new  $\{\text{Mo}_{248}\}$  cluster defining a hollow sphere (*figure 11*) [39]. The process corresponds to molecular nucleation (term used here not in the sense of crystal growth) under confined conditions.

#### Assembling spheres and wheels in different phases

In what follows, the assembling of spheres and wheels will be considered, which can lead to nano-objects of various size and dimensionalities.

#### • Solid phase

The neutral capsules of the type  $\{\text{Mo}_{72}\text{Fe}_{30}\}$  can be crosslinked. It has to be stressed that this solid-state reaction occurs at room temperature. Regarding the mechanisms leading to Fe-O-Fe bonds, there is a similarity to the well known inorganic condensation reactions in aqueous solution leading to polycations like in the case of  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ , for which a chaotic reaction occurs leading to amorphous products. This is no longer possible when it occurs with giant spheres. The discrete clusters present in the wet freshly filtered crystals approach one another then finally get linked during drying (*figure 12*) [63]. Each cluster in the final product is covalently linked to four other units through Fe-O-Fe bridges in a two-dimensional layer. The possibility of forming a related one-dimensional chain (paramagnetic Keplerate “necklaces”) from similar spherical nanospheres in a room-temperature reaction also exists [64].

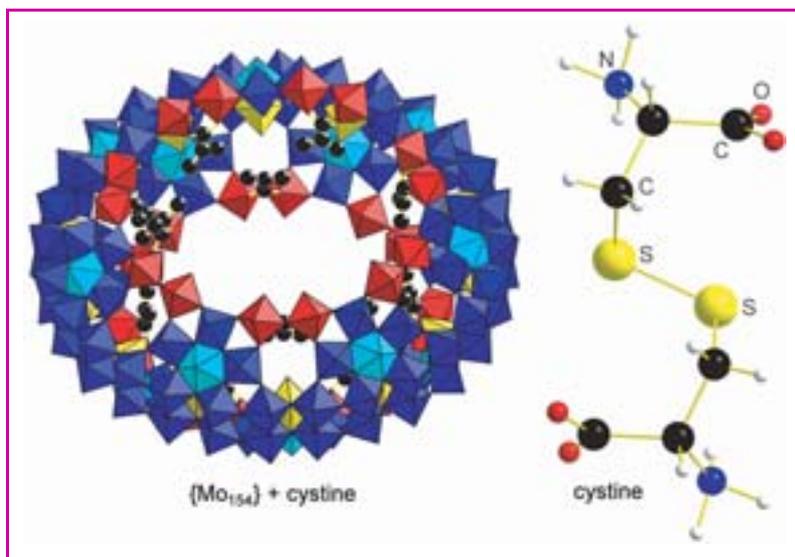


Figure 10 - Endohedral functionalization of the inner surface of a wheel-shaped  $\{\text{Mo}_{154}\}$  type nanocluster by cystine ligands (polyhedral representation, carboxylate group in ball-and-stick) [60].

The complete structure of the cystine ligands could not be found in the crystal structure but there is spectroscopic evidence for their integrity.

#### • Gas phase

As the  $\{\text{Mo}_{72}\text{Fe}_{30}\}$  spheres are neutral, it is possible to “kick them out” into the gas phase. Using matrix-assisted laser desorption and ionization (MALDI) methods, clusters, from dimers to pentamers, can be detected [65].

#### • Liquid phase

The wheel-shaped  $\{\text{Mo}_{154}\}$  anions assemble in aqueous solution, thus generating hollow spherical vesicles [66a], a result which was highlighted as “Rounding up nanoclusters” and “Metal-oxide nanowheels roll up into vesicles” [66b]. Static and dynamic light scattering data, as well as transmission and scanning electron microscopy, revealed hollow spheres with an average hydrodynamic radius of about 45 nm and comprising approximately 1,200 individual clusters (*figure 13*). The clusters appear to lie flat and homogeneously distributed on the vesicle surface, without touching each other. They are supposed to be held together by a balance of long-range electrostatic repulsion, short-range van der Waals attraction, and hydrogen bonding involving water molecules between the clusters. Furthermore the cations ( $\text{H}^+$  and  $\text{Na}^+$ )

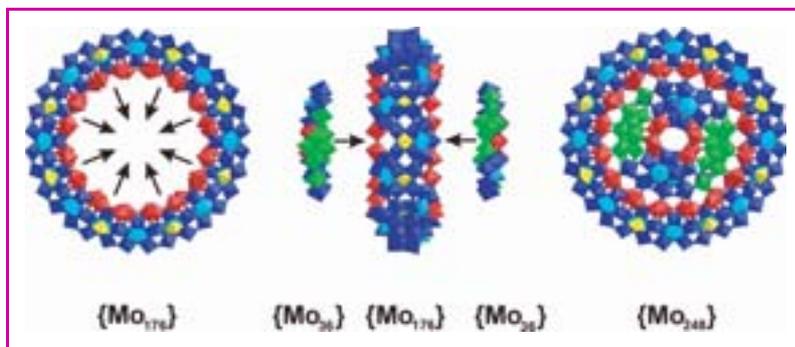


Figure 11 - Nucleation process under confined conditions: addition of two  $\{\text{Mo}_{36}\}$  “hub-caps” to the inner surface of the  $\{\text{Mo}_{176}\}$  type wheel leads to the formation of the  $\{\text{Mo}_{248}\}$  cluster [39].

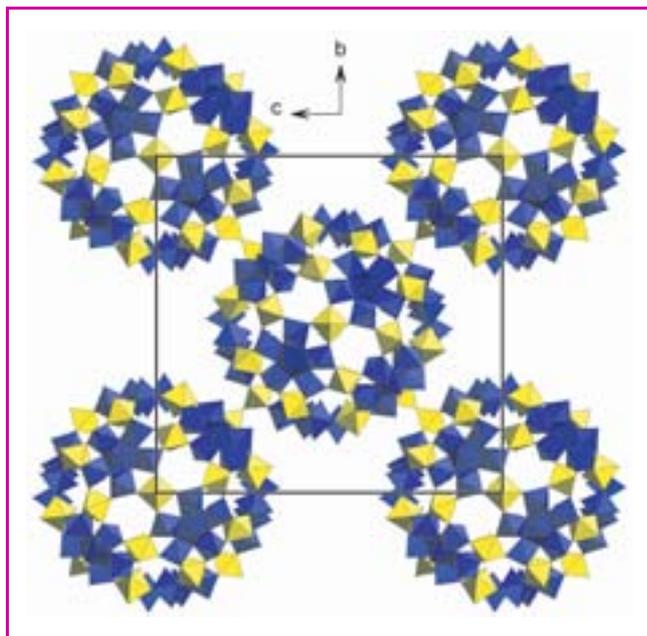


Figure 12 - An unprecedented solid-state reaction at room temperature.

Crosslinking neutral spherical nanoclusters of the type  $\{[(\text{Mo})\text{Mo}_5]_{12}(\text{Fe}^{\text{III}})_{30}\}$ , indicated by two  $\text{FeO}_6$  octahedra sharing corners, leads to the formation of a layered structure based on an unusual solid-state reaction at room temperature [63].

act as “glue” between the negatively charged wheels. Also  $\{\text{Mo}_{72}\text{Fe}_{30}\}$  sphere-type clusters show assembly processes in water [67]. Furthermore, evidence for the construction of oligomers/hybrids of the  $\{\text{Mo}_{132}\}$  keplerate in aqueous solution has been obtained by TEM studies of precipitates [68].

## Applications in materials science

Due to their multifunctional properties and their easy preparation methods [40], nanostructured ring- or ball-shaped polyoxomolybdates are attractive components for the construction of advanced nanodevices such as nanoreactors and sensors. One challenge in developing POM-based devices (e.g. electrochromic materials) is to integrate POMs into thin films of well-defined compositions and dimensions. One method to obtain thin films incorporating POMs is based on the properties of surfactant-encapsulated clusters. The surfactant shell improves the *stability* of the encapsulated cluster against *fragmentation*, enhances the *solubility* in nonpolar, aprotic organic solvents, neutralizes their *charge*, thus leading to discrete, *electrostatically neutral* assemblies, while altering the *surface chemical properties* (e.g. self-aggregation, surface adhesion, wetting behavior) in a predictable manner. Thus Kurth and co-workers have synthesized and characterized a surfactant-encapsulated  $\{\text{Mo}_{132}\}$  Keplerate which is quite attractive from a materials viewpoint [69].

Antonietti and co-workers have incorporated the spherical  $\{\text{Mo}_{132}\}$  and the wheel-shaped  $\{\text{Mo}_{154}\}$  species into sol-gel-derived silica where they remain accessible for reactions in the gas phase or even in solution [70]. They also have shown that  $\{\text{Mo}_{154}\}$ -surfactant complexes self-assemble towards 3-D structures with liquid crystal behaviour [71]. In another field of application, Liu and co-workers have synthesized single-walled carbon nanotubes using the  $\{\text{Mo}_{72}\text{Fe}_{30}\}$  capsules with encapsulated Keggin ions as patterning catalysts [72].

Generally speaking, POMs can be considered as a potential class of (supra)molecular modules (SUMOs) for functional devices and materials. As a matter of fact they represent well-defined, discrete nanoscopic clusters with a large variety of applications in fundamental and applied science including catalysis, electrochemistry, electrooptics, medicine, corrosion protection dyes and pigments, dopants in (non-)conductive polymers and sol-gels, bleaching of paper pulp, as well as analytical chemistry (see [69b, 73] and literature cited therein).

## Conclusions and interdisciplinary perspectives

This review provides a survey of polyoxometalate chemistry with special emphasis on its history, with particular attention to Souchay's and Müller's contributions. Souchay paved the way and brought clarity into a field which had largely remained confused before him. Müller then took over and unraveling the mystery of Mo blues elegantly started the rational design of clusters of increasing size ranging from ca. 1 to 6 nm.

In the last 15 years, the field has produced remarkable nano-objects on the route “from simplicity to complexity”. *Figure 14* dramatically illustrates this aspect: the latest clusters have now macromolecular dimensions with a size similar to that of the protein Human Carbonic Anhydrase II [73]. It is important to note that only molybdenum oxide-based

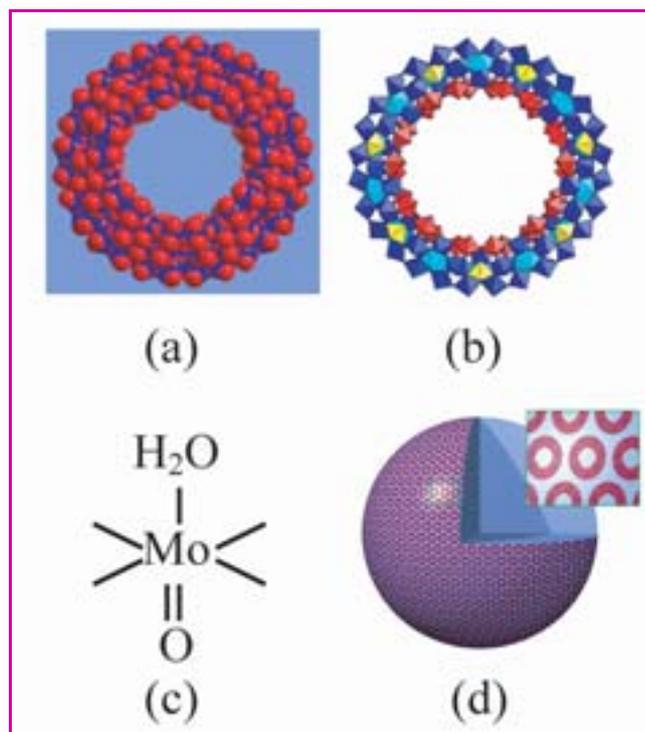


Figure 13 - A new state of ions in solution: structure of the 3.6 nm size  $\{\text{Mo}_{154}\}$  type nanowheel with a hydrophilic surface and nanosized central cavity as well as the related vesicle.

(a) Space-filling representation (Mo atoms blue and light blue; O atoms red). (b) Polyhedral representation, demonstrating the abundance of pentagonal  $\{(\text{Mo})\text{Mo}_5\}$  units (in blue) probably influencing the water structure ( $\{\text{Mo}_2\}$  units red;  $\{\text{Mo}_1\}$  units yellow). (c) The typical smallest fragment with a metal atom and its coordination sphere, i.e. with one of the 70  $\text{H}_2\text{O}$  ligands causing the extreme hydrophilic nature that is responsible for the interaction with solvents such as water. (d) Schematic plot of the vesicle structure ( $\approx 45$  nm radius) formed from ca.  $12 \times 10^2$  nanowheels in aqueous solution; the inset shows enlarged nanowheels [66a].

systems under reducing conditions show the presently described unique variety of structures and molecular assembly processes. The versatile reactivities of these nanosized species depend not only on their specific type of internal and external surface functionality, but also on their size, as well as their form.

With respect to the molecular wheels, the “torus” cavity allows to create novel internal surface functionalities by the incorporation of multiphilic ligands like cystine. Importantly, the internal surface reactivity depends on the cavity size, as shown by the different behaviour of the  $\{\text{Mo}_{154}\}$  and  $\{\text{Mo}_{176}\}$  wheels. Noncovalent, e.g. the incorporation of zinc porphyrins [74] and the partly covalent integration of a 64-membered ring comprising 16  $\text{K}^+$  and 16  $\text{SO}_4^{2-}$  ions [61] into the larger  $\{\text{Mo}_{176}\}$  ring, as well as covalent interactions leading to the closing of the cavity of the  $\{\text{Mo}_{176}\}$  ring with two  $\{\text{Mo}_{36}\}$  type caps [39] can be observed, as discussed in detail above.

The capsules are particularly interesting for chemistry and materials science because they present a large variety of active recognition sites on the outer and innermost surface as well as at the pores and channels. Interactions with their environment have been discussed in paragraphs “Specific interactions” and “Applications”, which may lead to future developments considered below.

### Encapsulation and related nano-separation chemistry

This type of biomimetic chemistry concerns studies on nanomaterials encapsulating a range of liquids, including water with or without electrolytes [59c] and may give valuable information, e.g. on highly constrained water in the living cell. The capsules can separate/position uptaken cations like a nano-ion chromatograph. Furthermore, reactions can be performed inside the  $\{\text{Mo}_{132}\}$  cluster, e.g. at reactive ligands coordinated to  $\text{Mo}^{\text{V}}_2$  linkers like anions dicarboxylic acids with one free carboxylic acid function, but also in the smaller  $\{(\text{Mo})\text{Mo}_5\}_{12}\{\text{Fe}^{\text{III}}\}_{30}$  capsule, by replacing the  $\text{H}_2\text{O}$  ligands coordinated at the Fe-linkers for instance by NO molecules. A variety of spectroscopic and magnetic studies can be performed on protected metal complexes with (encapsulated) water shells acting as polydentate ligands, and more broadly on nanosized materials. This type of approach has been highlighted [75] also with reference to works of Rebek [76] and Fujita [77].

### Artificial cell - environment interactions

Nature’s pathways can be modelled using the capsules as artificial cells, such as (i) ion uptake-and-release processes through membranes, and (ii) cell response to stimuli, such that pore closing by molecules acting as corks/“stimuli” significantly influence the structure of encapsulates. For instance, (i) provides the possibility for modelling the opening and blocking of gates/pores and ionic mobility through channels, which play a key role in several biological information transfer processes. It is thus no surprise if Nina Hall entitled her highlight on Müller’s work “Bringing inorganic chemistry to life” [33].

### Modelling oxide surfaces

Because capsules possess pores, the comparison with the building units of zeolites (supercages or sodalites) naturally comes to mind. Thus the spherical cluster  $\{\text{Mo}_{132}\}$  has pores of ca. 0.5 nm in diameter, comparable to those of fau-

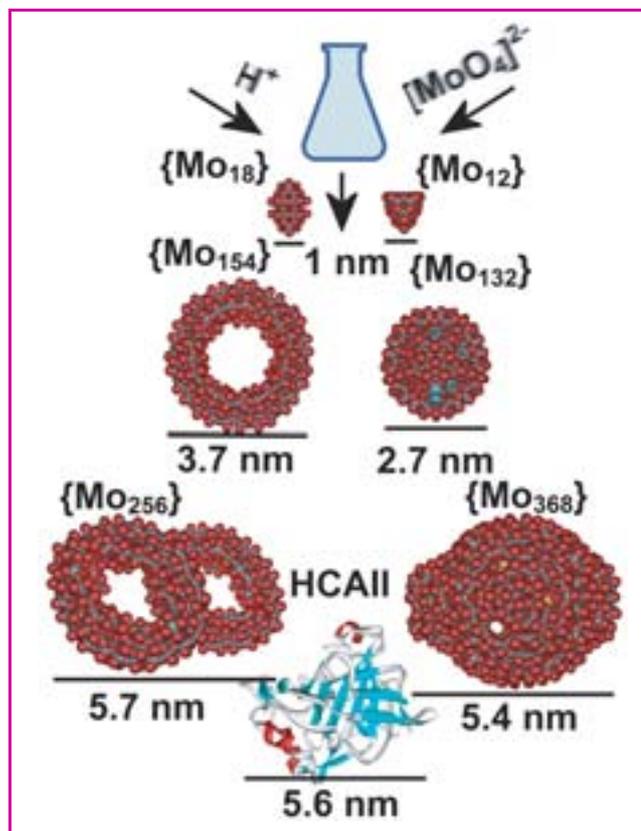


Figure 14 - Representations of the structures of some polyoxomolybdate clusters, all synthesized under “one-pot” acidic reaction conditions, from the Keggin  $[\text{XMo}_{12}\text{O}_{40}]^{\text{I-}}$  and Dawson  $[\text{X}_2\text{Mo}_{18}\text{O}_{62}]^{\text{I-}}$  anions to the  $\{\text{Mo}_{154}\}/\{\text{Mo}_{132}\}$  and  $\{\text{Mo}_{256}\}/\{\text{Mo}_{368}\}$  clusters (space filling models, Mo: green, O: red). These clusters are compared (to scale) with the protein Human Carbonic Anhydrase II. The figure was kindly provided by Dr. L. Gronin [73].

jasite-type zeolites. The  $\{\text{Mo}_9\text{O}_9\}$  pores of the  $\{\text{Mo}_{132}\}$  capsule have crown-ether function like the  $\{\text{T}_6\text{O}_6\}$  pores ( $\text{T} = \text{Si}, \text{Al}$ ) of sodalite cages of faujasite-type zeolites [78]. In contrast to zeolites, molybdenum oxide-based nanoclusters have acid as well as redox centres ( $\text{Mo}^{\text{V/VI}}$ ), but are also electron-rich, which are key characteristics to promote catalytic reactions.

Another interesting comparison can be made, this time with layered solids, for instance when  $\{\text{Mo}_{154}\}$  clusters are linked to form layered frameworks with nanosized channels [79]. The problem not been solved yet is the removal of cations inside the channels of the wheels so that the internal surface cannot be increased. In this context, it should be mentioned that it is still a challenge to understand details of the interaction (mechanisms) of substrates with the surfaces of heterogeneous catalysts, as for instance in the case of transition metal oxides which play a key role in industrial processes, e.g. in selective oxidations.  $\text{MoO}_3$  is of particular interest because it exhibits very versatile catalytic properties. A tremendous step to this end would be to consider the well defined discrete giant metal-oxide based cluster species, i.e. nanoreactors (which show the same or a similar structure including defects on their large surfaces), as relevant for catalytically active bulk materials, the surface of which is difficult to investigate. Remarkably, not much is known about the influence of such defects present on the surface of an oxide, and their role in determining the catalytic properties. These defects can be generated on the basis of the  $\{\text{Mo}_{154}\}$  type cluster ([80] and references therein).

A final remark should be related to magnetism. This concerns the unique  $\{(Mo^V)Mo_5\}_{12}(M^m)_{30}$  type antiferromagnets ( $M = Fe(III), V(IV)$ ) and showing a novel type of frustration which can be used to model the celebrated Kagomé lattices [81] (note that they contain linked triangles causing frustration). The latter play a role in materials science [82].

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### Historical note

The cover picture shows the first page of the original paper of Scheele about Molybdenum Blue (1778) as well as the cover page of the related issue. Interestingly the paper was translated from the Swedish into the French and included under the title "Sur la Mine de Plomb ou Molybdène" in the series of "Observations sur la Physique, sur l'Histoire Naturelle et sur les Arts" by M. L'Abbé Rozier et M. J.A. Mongez le jeune, which collects important scientific publications of that time. It is striking to see that chemistry had already a European dimension at that time.



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