Advanced Functional Inorganic POMs, Coordination Clusters and Framework Materials

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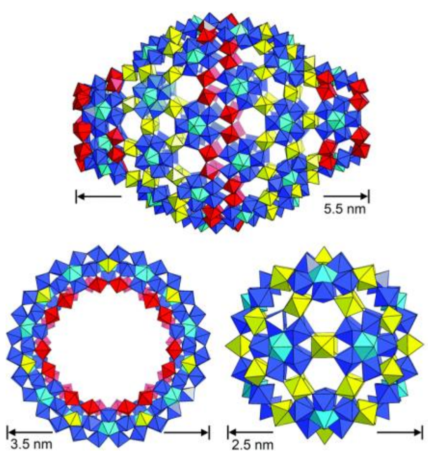
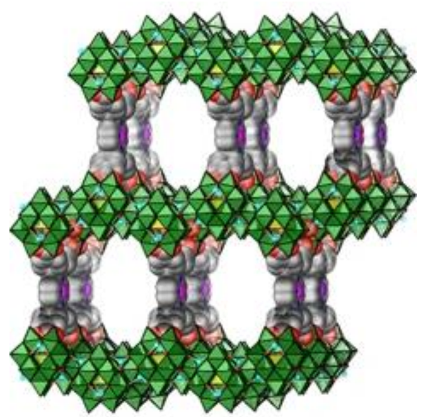
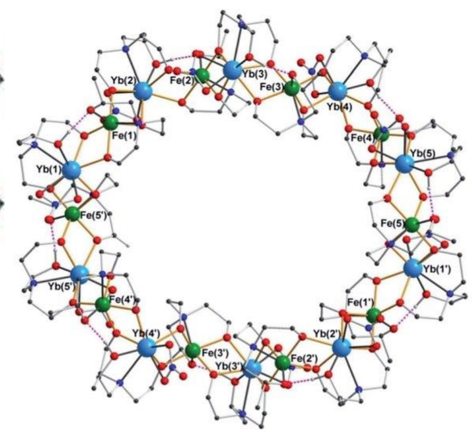
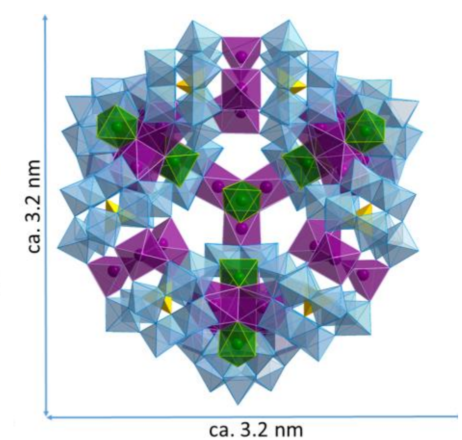
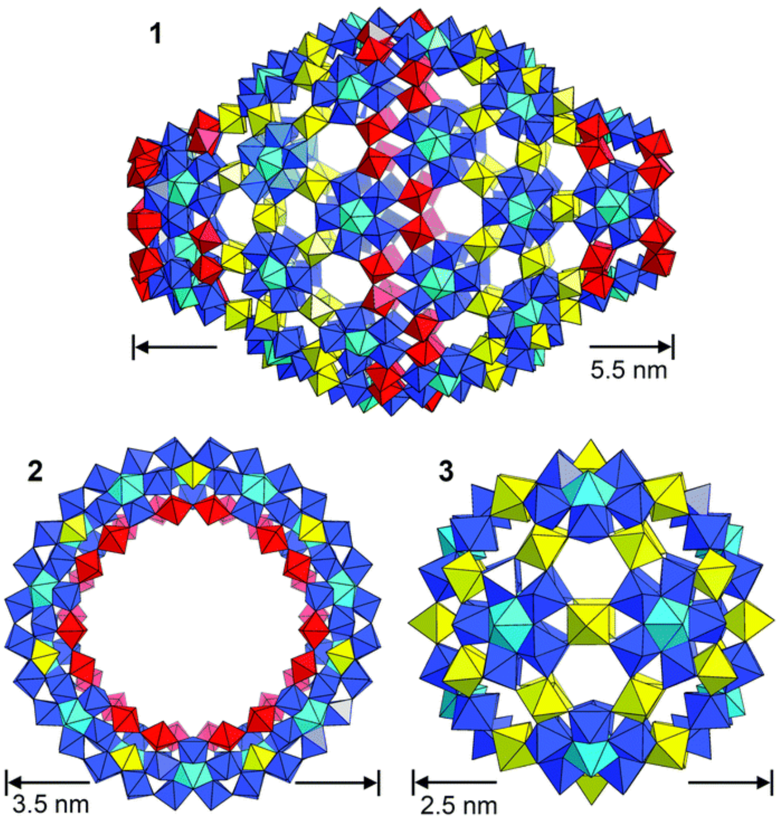








Polyoxomolybdates: Molybdenum Blues (MBs)



A special class of polyoxomolybdates: Molybdenum blue structural types

Solutions of molybdenum blues (MBs) was first mentioned by Scheele in 1783

C. W. Scheele, ed. Martin Sändig, Niederwalluf/Wiesbaden (reprint: original 1793), Vol. 1, 1971.

$\{Mo_{368}\}$-Lemon $[H_xMo_{368}O_{1032}(H_2O)_{240}(SO_4)_{48}]^{48-}$ **(1)**
$\{Mo_{154}\}$-Wheel $[Mo^{VI}_{126}Mo^{V}_{28}O_{462}H_{14}(H_2O)_{70}]^{14-}$ **(2)**
$\{Mo_{102}\}$- Sphere $[\{Mo_6O_{21}(H_2O)_3(SO_4)\}_{12}(MoO(H_2O))_{30}]$ **(3)**

A. Müller, E. Krickemeyer, J. Meyer, H. Bögge, F. Peters, W. Plass, E. Diemann, S. Dillinger, F. Nonnenbruch, M. Randerath, C. Menke, *Angew. Chem. Int. Ed*., 1995, 34, 2122-2124.
A. Müller, E. Beckmann, H. Bögge, M. Schmidtmann and A. Dress, *Angew. Chem. Int. Ed* Angew. 2002, 41,1162-1167.
A. Müller, B. Botar, S. K. Das, H. Bögge, M. Schmidtmann and A. Merca, *Polyhedron*, 2004, 23, 2381-2385.

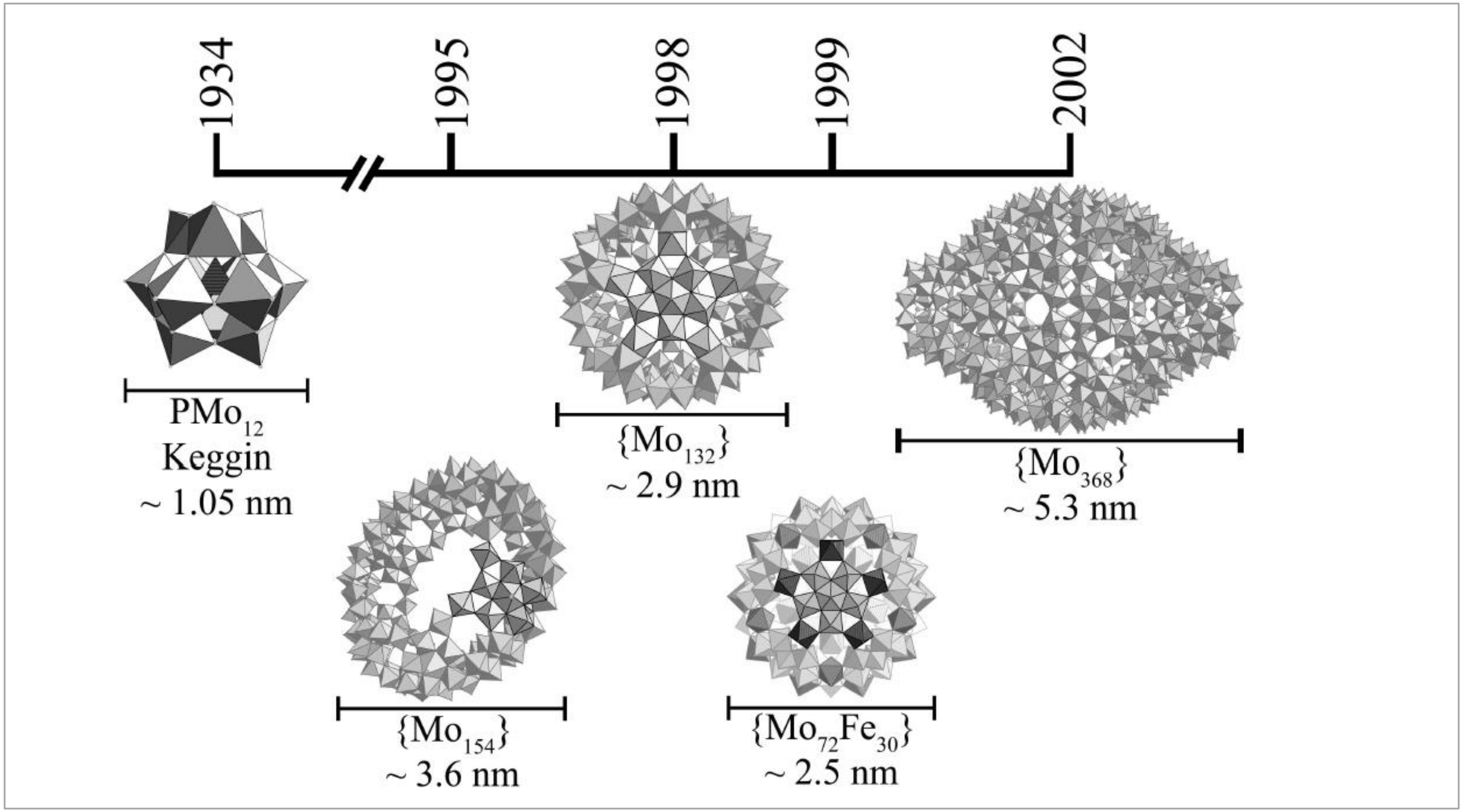
History of Molybdenum Blues (MBs)

The history of polyoxomolybdates dates back centuries ago with the famous **blue waters** observed by Native Americans near today's Idaho Springs in the Valley of the Ten Thousand Smokes.

The existence of highly reduced molybdenum oxide species was reported as early as **1783** when **C. W. Scheele** observed the formation of a deep blue solution upon heating molybdenum (VI) oxide, MoO_3, in concentrated nitric acid.

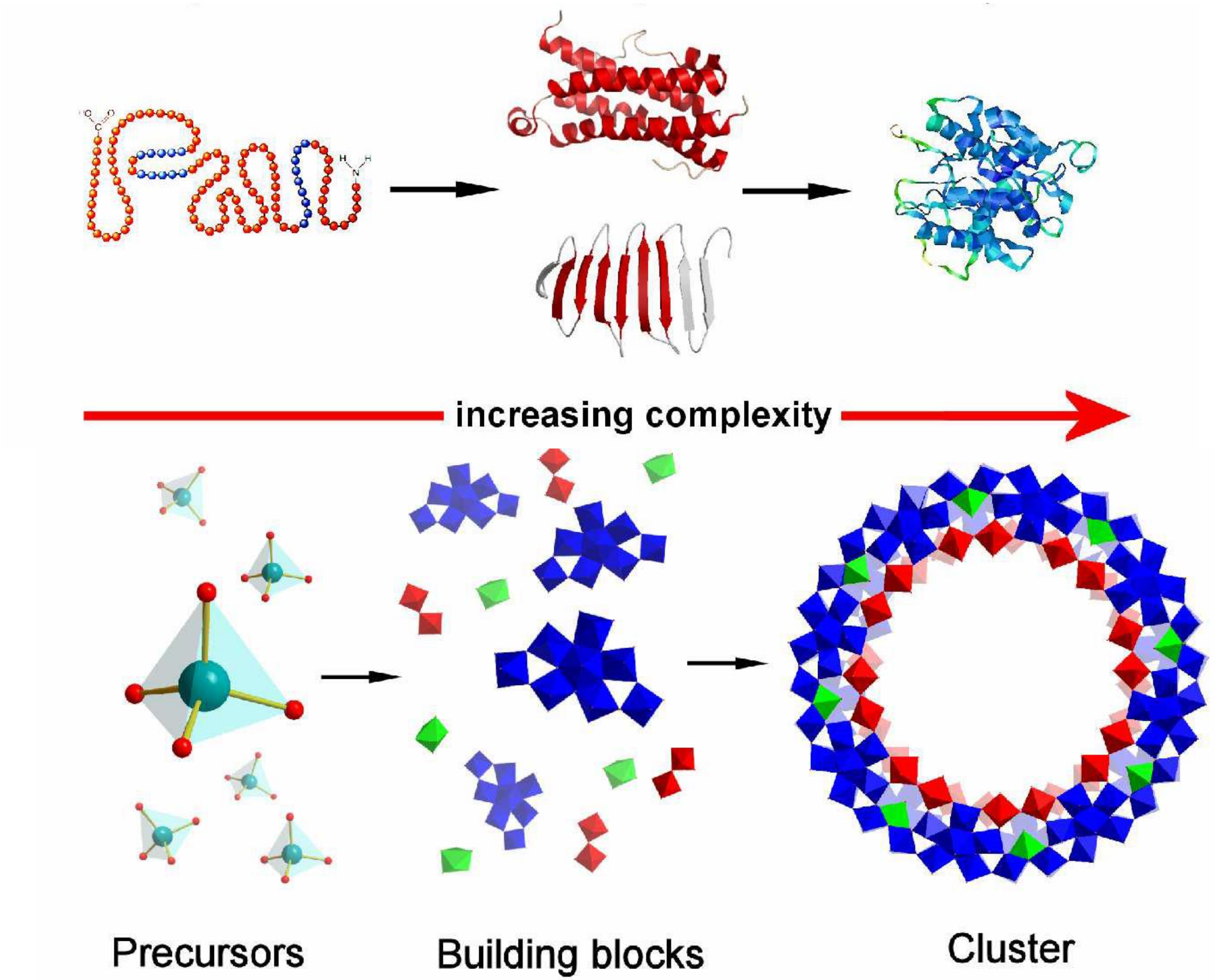
L. Gmelin. Gmelin Handbuch der Anorganischen Chemie.Molybdan. Springer-Verslag, Berlin - Heidelberg - New York, 8th edition, 1935.
C. W. Scheele, Sämtliche physische und chemische Werke, (reprint, original: 1793) ed., Martin Sändig, Wiesbaden, 1971.

History of Molybdenum Blues (MBs)



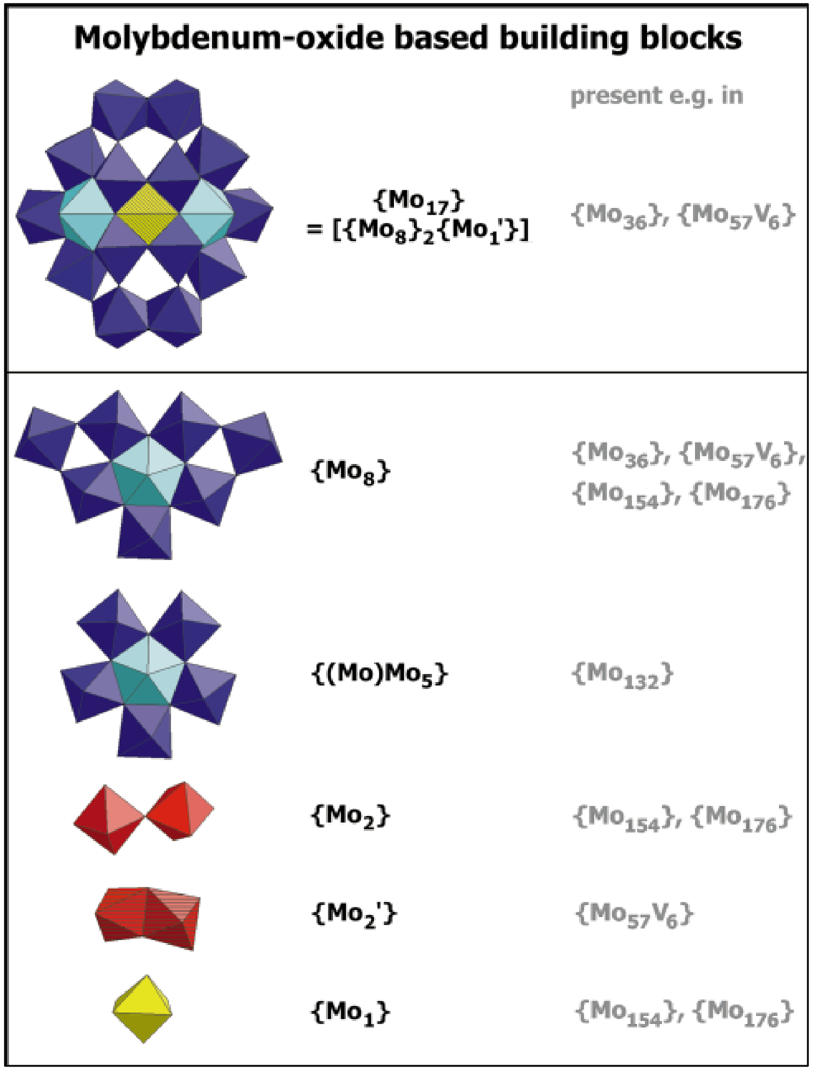
$\{Mo_{368}\}$ cluster with its 112 Mo(4d) electrons (*i.e.* an $Mo^{V}/(Mo^{V} + Mo^{VI})$ ratio of 30.4%) is considerably higher reduced than any wheel species. In contrast, all $\{Mo_{154}\}$-type species contain 28 Mo(4d) electrons; all $\{Mo_{176}\}$-type species contain 32 Mo(4d) electrons (18.2%)

Building Blocks



Streb, Carsten (2008) Functional polyoxometalate assemblies: from host-guest complexes to porous frameworks.

Nature and Variety of the Constituent Building Blocks



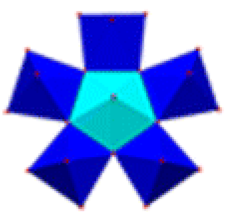
A. Müller, P. Kögerler, C. Kuhlmann, *Chem. Commun.*, 1999, 1347-1358.

Structural Types: [(pent)$_{12}$(link)$_{30}$] Type Spherical Clusters

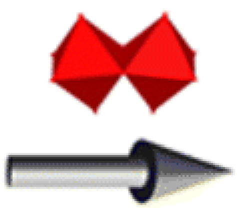
Development of Keplerate-type chemistry

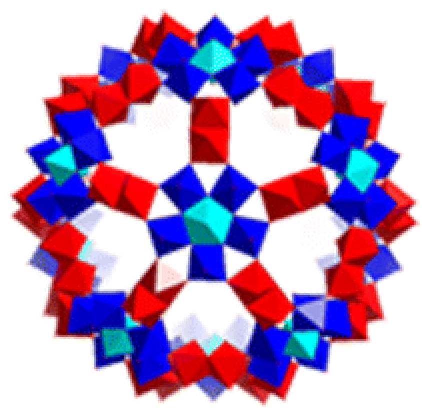
{Mo_{132}}- Sphere

- A class of MB which form POM-shells in solution
- Highly symmetric, hollow, spherically shaped
- They consist of 12 five-fold building blocks or pentagons which are linked together to form a sphere, similar to soccer ball.



Pentagonal {$(Mo^{VI})Mo^{VI}_5$}

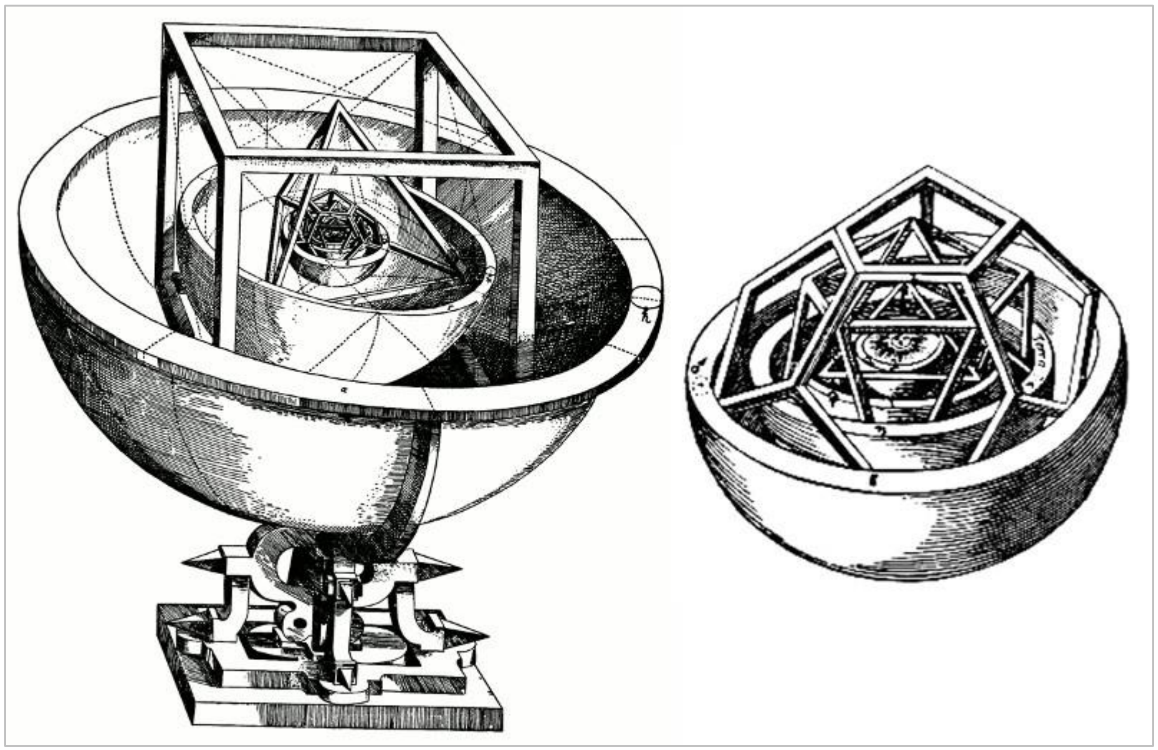




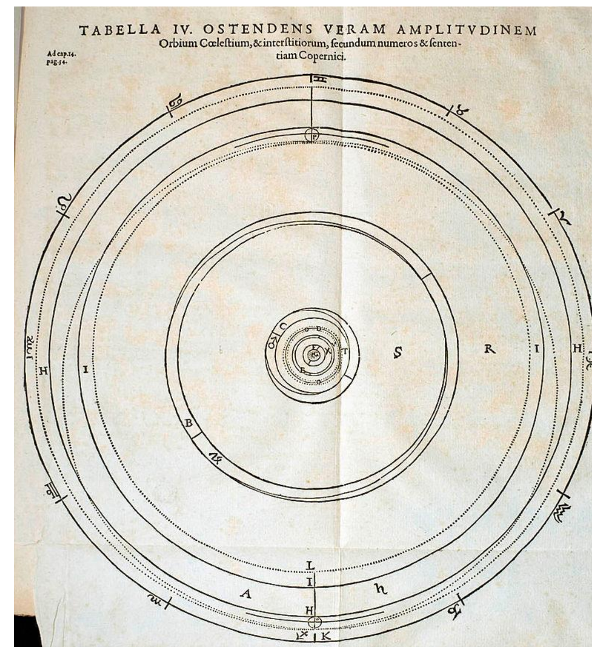
$[(Mo^{VI}(Mo^{VI})_5O_{21}(H_2O)_6)_{12}(Mo^{V}_2(\mu\text{-}O)_2O_2)_{30}]^{12-}$

Structural Types: Keplerates

The name **Keplerate** was first introduced by Müller.The term comes from Johannes **Kepler**, a 17th century mathematician, astronomer and astrologer.



Kepler's Platonic solid model of the Solar System from Mysterium Cosmographicum (1596) from Kepler’s book. Detail of inner four planets is on the right.



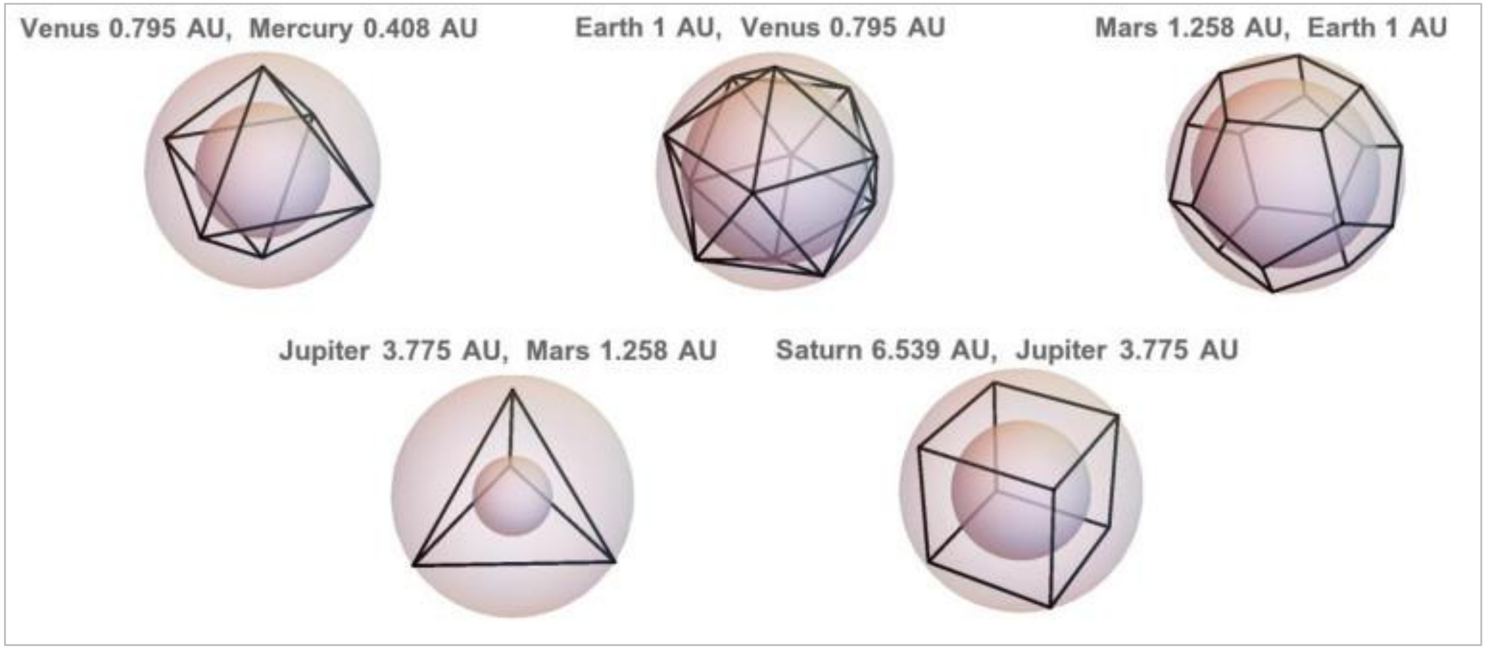
Johannes Kepler's diagram of the celestial spheres, and of the spaces between them, following the opinion of Copernicus (*Mysterium Cosmographicum*, 2nd ed., 1621)

Keplerates

There were only 6 known planets at the time.

Mercury — Venus — Earth — Mars — Jupiter — Saturn

The six planets from Mercury out to Saturn were separated by the solids in the sequence octahedron, icosahedron, dodecahedron, tetrahedron and cube. The Sun was at the centre of the six concentric spheres.



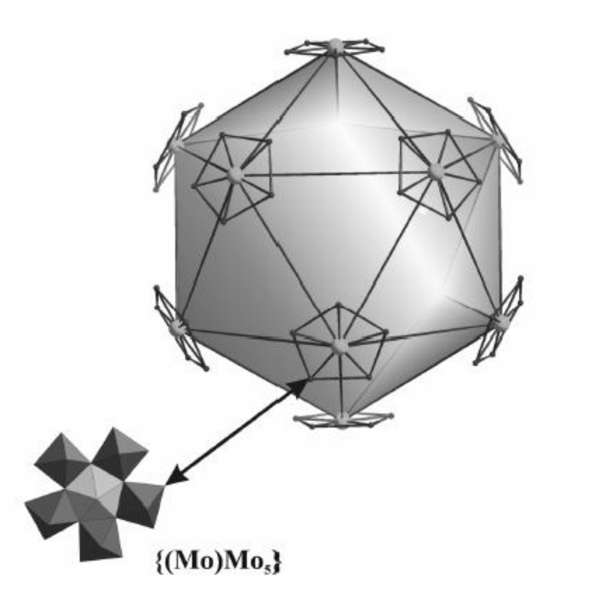
Keplerates

Average Distance of the Planets from the Sun		
Planet	**Average Distance (km)**	**Average Distance (AU)**
Mercury	57,910,000	0.39
Venus	108,210,000	0.72
Earth	149,600,000	1.00
Mars	227,920,000	1.52
Jupiter	778,570,000	5.20
Saturn	1,433,530,000	9.58
Uranus	2,872,460,000	19.20
Neptune	4,495,060,000	30.05

Development of Keplerate-Type Chemistry

All such spherical clusters, which can be described by the general formula **$[\{(Mo)Mo_5\}_{12}\{L\}_{30}]$** or **$[(pentagon)_{12}(linker)_{30}]$,** belong to the family of "**Keplerate**" type molecules because of their similarity to Kepler's early model of the Universe.

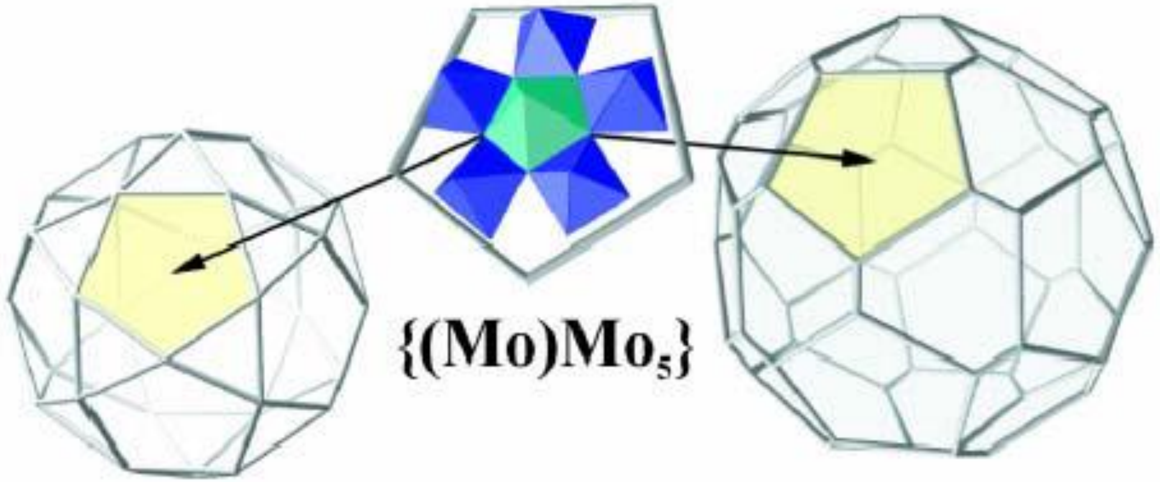
L= $\{Fe^{III}(H_2O)\}^{3+}$, $\{Mo^{V}O(H_2O)\}^{3+}$, $\{V^{IV}O(H^2O)\}^{2+}$, or $\{Mo^{V}_2O_4(ligand)\}^{n+}$ (e.g. ligand = $HCOO^-$, CH_3COO^-, SO_4^{2-}, $H_2PO_2^-$, PO_4^{3-}),



The basis for the formation of the **$[(pentagon)_{12}(linker)_{30}]$** type clusters. **$[(Mo)Mo_5]$** units define the icosahedron vertices.

Development of Keplerate-Type Chemistry

"Sizing" the nanospheres is possible

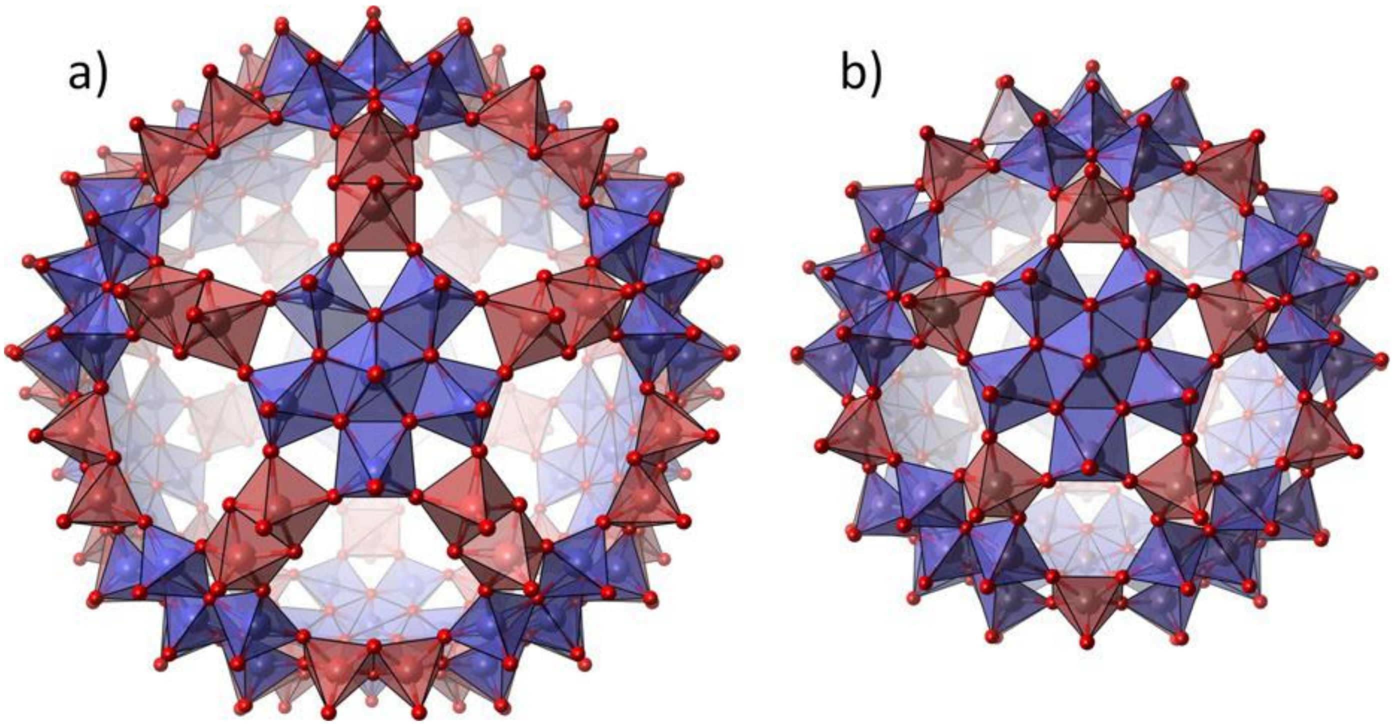


Left: the icosidodecahedron with **12 pentagons** and **20 triangles** formed by **mononuclear linkers**.
Right: the (distorted) truncated icosahedron with twelve pentagons and twenty hexagons formed by 30 **dinulear [Mo_2] linkers**

A. Müller and P. Gouzerh , *Chem. Soc. Rev.*, 2012, **41** , 7431-7463

Development of Keplerate-Type Chemistry

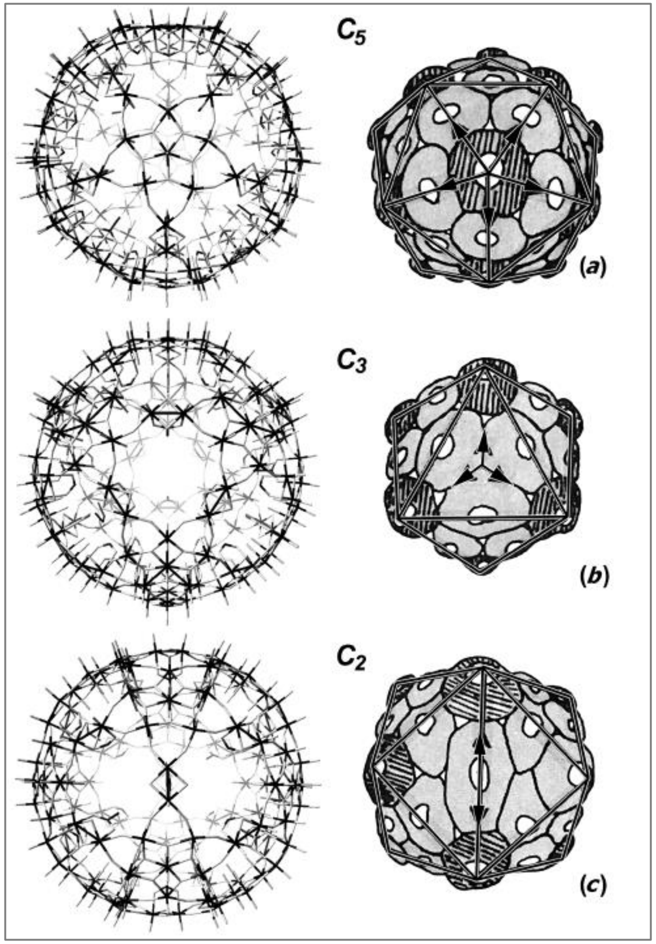
"Sizing" the nanospheres is possible



(a) Mo_{132} and (b) Mo_{102}. Pentagonal motifs are represented in blue and are equivalent for both systems.

A. Müller and P. Gouzerh , *Chem. Soc. Rev.*, 2012, **41** , 7431-7463

$\{Mo_{132}\}$- MB cluster: A Topological Model For Spherical Viruses

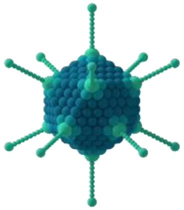


For the purpose of comparison, corresponding schematic representations of an icosahedral virus capsid (*T* = 3) with 20 hexagonal and 12 pentagonal capsomers (morphology units) are presented.

(a) In both systems, the C_5 axes cross the centers of the pentagonal units (hatched)

(b) The C_3 axes cross the midpoint between three units

(c) The C_2 axes cross the center of the units (*c*).

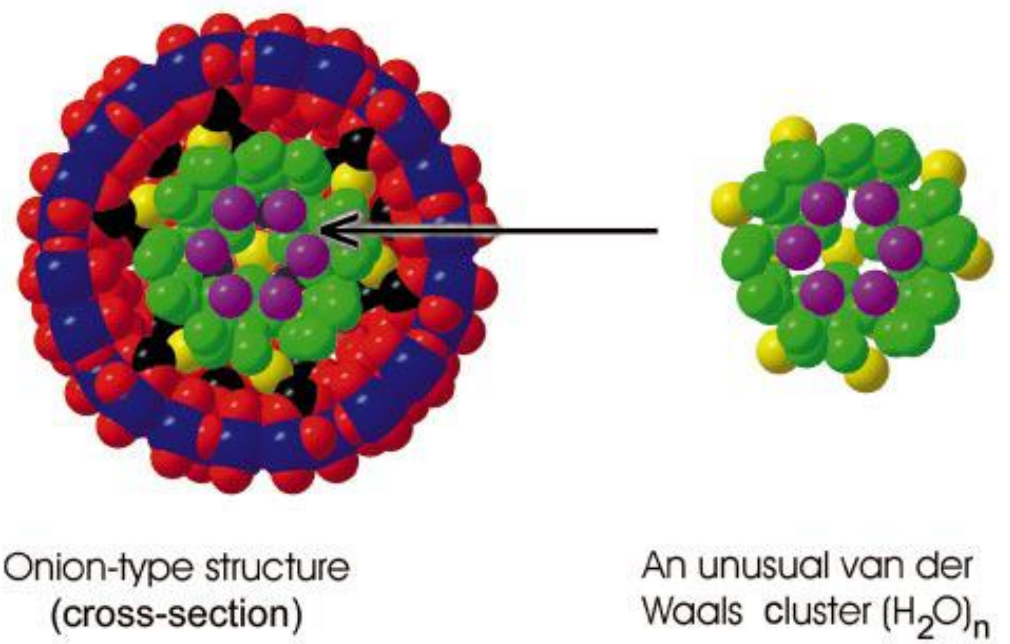


The icosahedral structure is extremely common among viruses

A. Müller, P. Kögerler, C. Kuhlmann, *Chem. Commun*., 1999, 1347-1358.

A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann and F. Peters, *Angew. Chem., Int. Ed.*, 1998, **37**, 3360.

Different Shells of Encapsulated H_2O Molecules



Cross section through the equator of $[(H_2O) @ Mo^{VI}_{72}Mo^{V}_{60}O_{372}(HCO_2)_{30}(H_2O)_{72}]^{42-}$ allowing a view into the cavity of the cluster shell and highlighting the hydrogen-bonded cluster formed by the encapsulated H_2O molecules (oxygen atoms)

(left) The different shells spanned by encapsulated H_2O molecules are represented by spheres with different colours [violet shell (radius ca. 3.5 Å), green shell (6.2–6.9 Å) and yellow shell (8.2–8.7 Å)

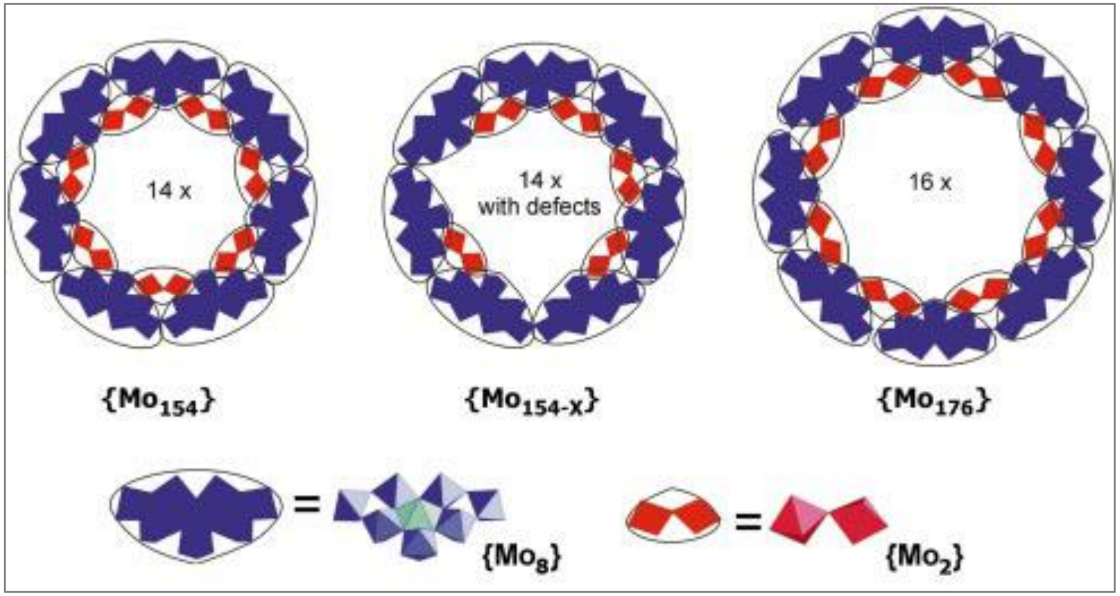
(right) The onion-like structure of the whole anion is completed by the three following outer shells consisting of (1) that of the 72 H_2O and 30 formate ligands coordinated to molybdenum atoms and pointing into the cavity (ca 10.5 Å), (2) that of the 132 molybdenum atoms (ca 13.1 Å) and (3) that of the terminal 132 oxygen atoms (ca 14.7 Å)

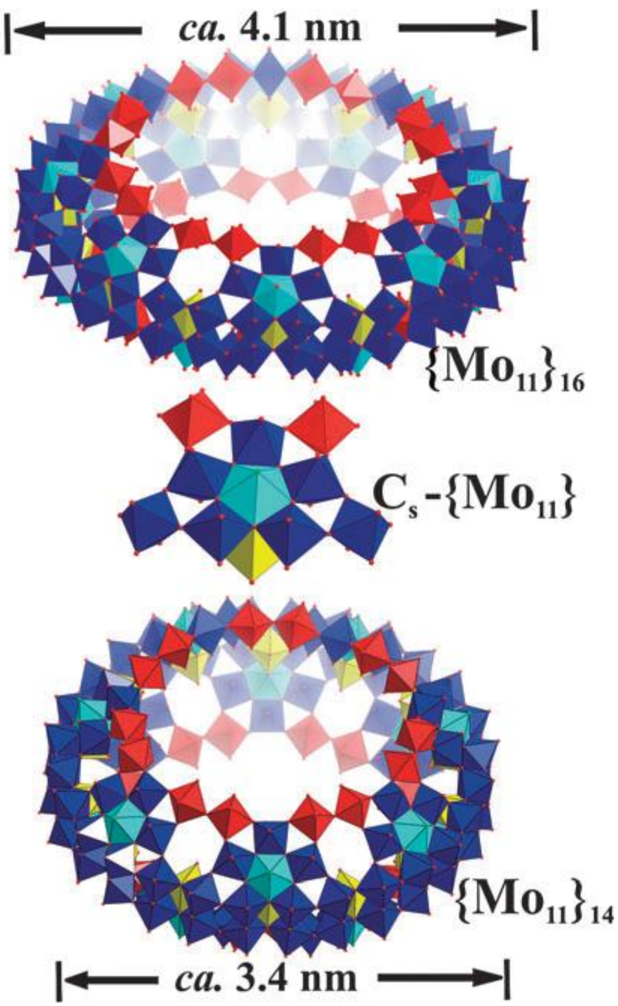
(Mo centers: blue, O atoms: red, C atoms: black).

A. Müller, P. Kögerler, C. Kuhlmann, *Chem. Commun.*, 1999, 1347-1358.

Structural Types: Giant Wheels

The Wheel-type structures can formally be represented as **$[\{Mo_8\}\{Mo'_2\}\{Mo_1\}]_n$ $\{Mo_{11}\}$** where **n = 14** and **16** for **$\{Mo_{154}\}$** and **$\{Mo_{176}\}$** respectively.

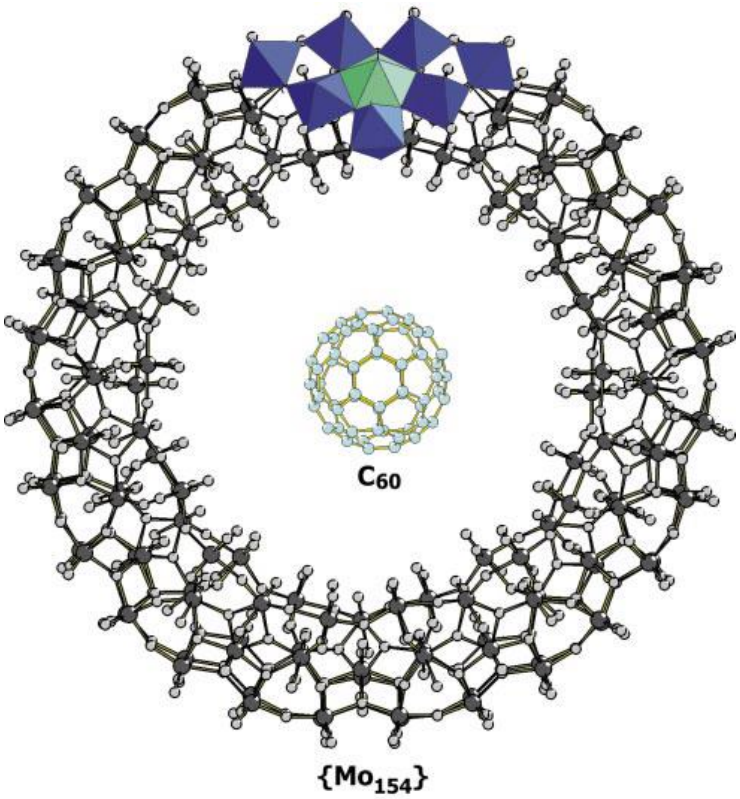




A. Müller and P. Gouzerh , *Chem. Soc. Rev.*, 2012, 41 , 7431-7463.
A. Müller, P. Kögerler, C. Kuhlmann, *Chem. Commun*., 1999, 1347-1358.

Structural Types: Giant Wheel $\{Mo_{154}\}$

$[Mo^{VI}_{126}Mo^{V}_{28}O_{462}H_{14}(H_2O)_{70}]^{14-}$

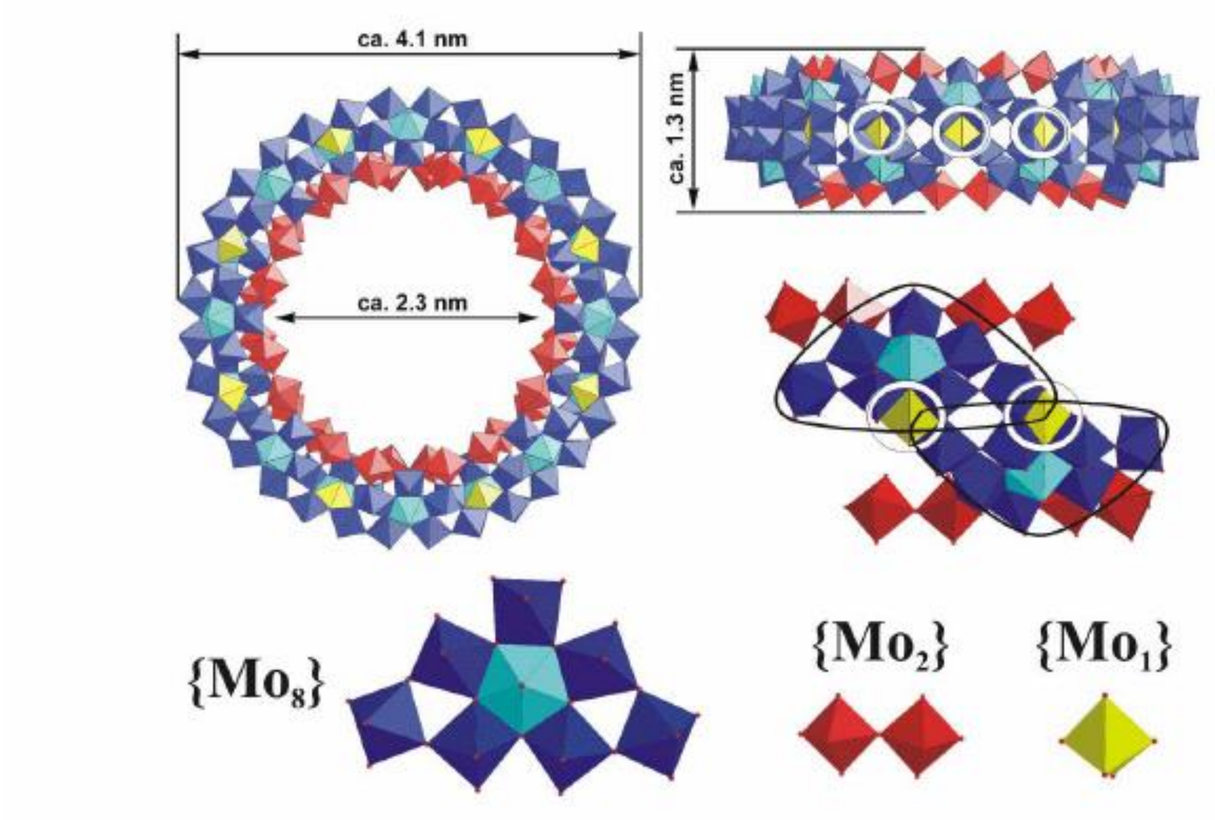


Showing one $\{Mo_8\}$ unit (blue) with its central MoO_7 pentagonal bipyramid (cyan) in polyhedral representation. For the purpose of size-comparison, a C_{60} fullerene molecule is shown.

A. Müller, P. Kögerler, C. Kuhlmann, *Chem. Commun*., 1999, 1347-1358.

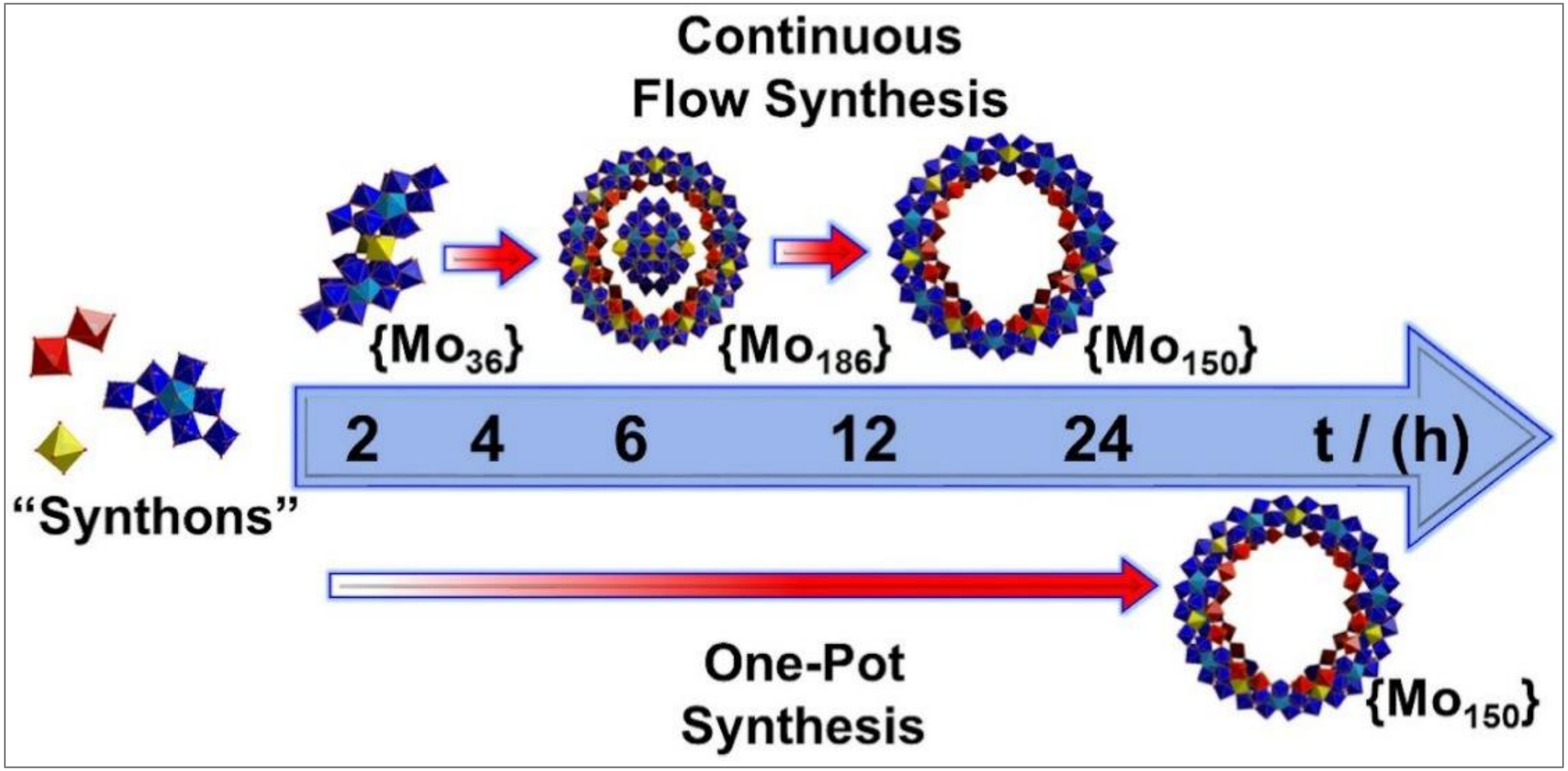
Structural Types: Giant Wheel $\{Mo_{176}\}$

$[Mo_{176}O_{528}H_{16}(H_2O)_{63}(CH_3OH)_{17}]^{16-}$



Hexadecameric cluster **$\{Mo_{176}\}$** cluster. The $\{Mo_8\}$, $\{Mo_2\}$ and $\{Mo_1\}$ building blocks are shown below and the positions of $\{Mo_1\}$ units are ringed on the side view on the right side.

Giant Wheels: Structure-Directing Template



Formation of $\{Mo_{186}\}$, $\{Mo_{150}\}$ and $\{Mo_{36}\}$ complexes. The flow-reaction conditions and the reducing environment are necessary factors for the isolation of $\{Mo_{36}\}$. Colour scheme, yellow: $\{Mo_{1}\}$, red; $\{Mo_{2}\}$, blue; $\{Mo_{8}\}$.

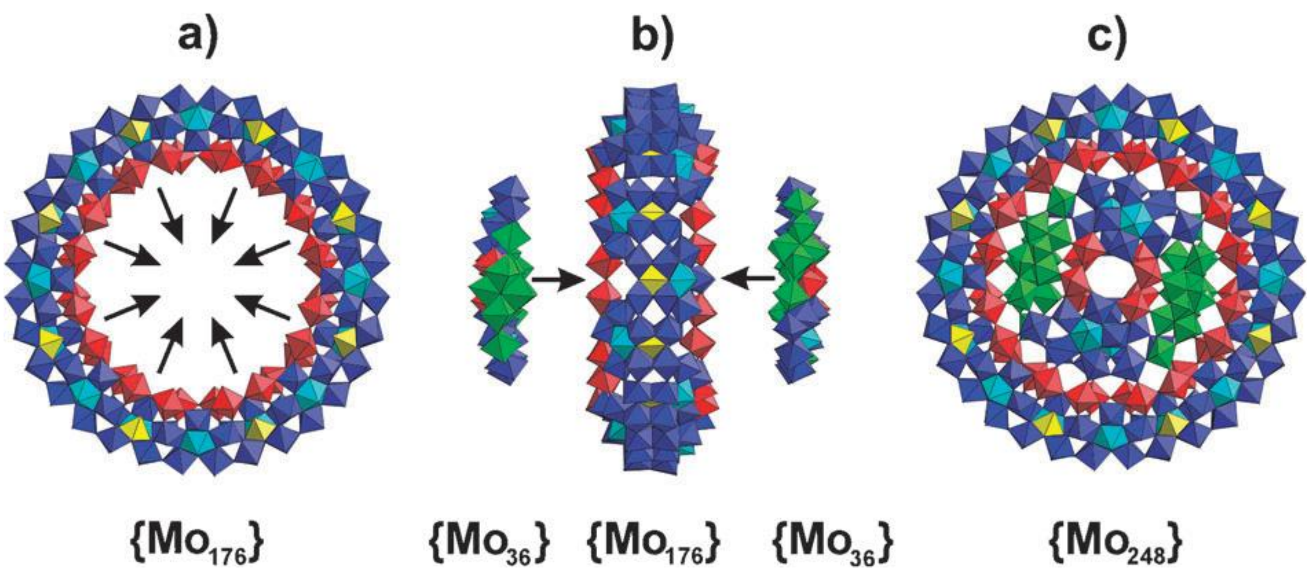
S. Passadis, T. A. Kabanos, Y. –F. Song, H. N. Miras, *Inorganics,* 2018, *6*, 71.

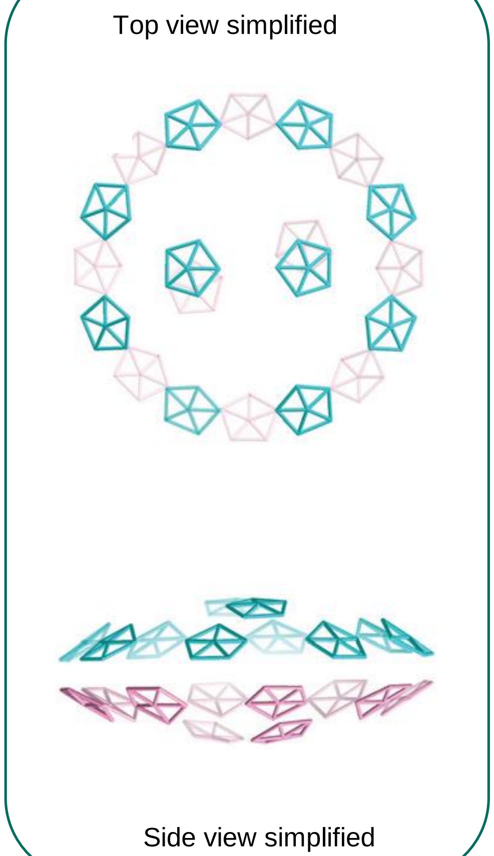
Giant Wheels: Molecular Growth

$[Mo_{248}O_{720}H_{16}(H_2O)_{128}]^{16-}$

$\{Mo_{176}\}$ to $\{Mo_{248}\}$ cluster

$\{Mo_{248}\} \equiv [\{Mo_2\}_{16}\{Mo_8\}_{16}\{Mo_1\}_{16}\{Mo_{36}\}_2]$





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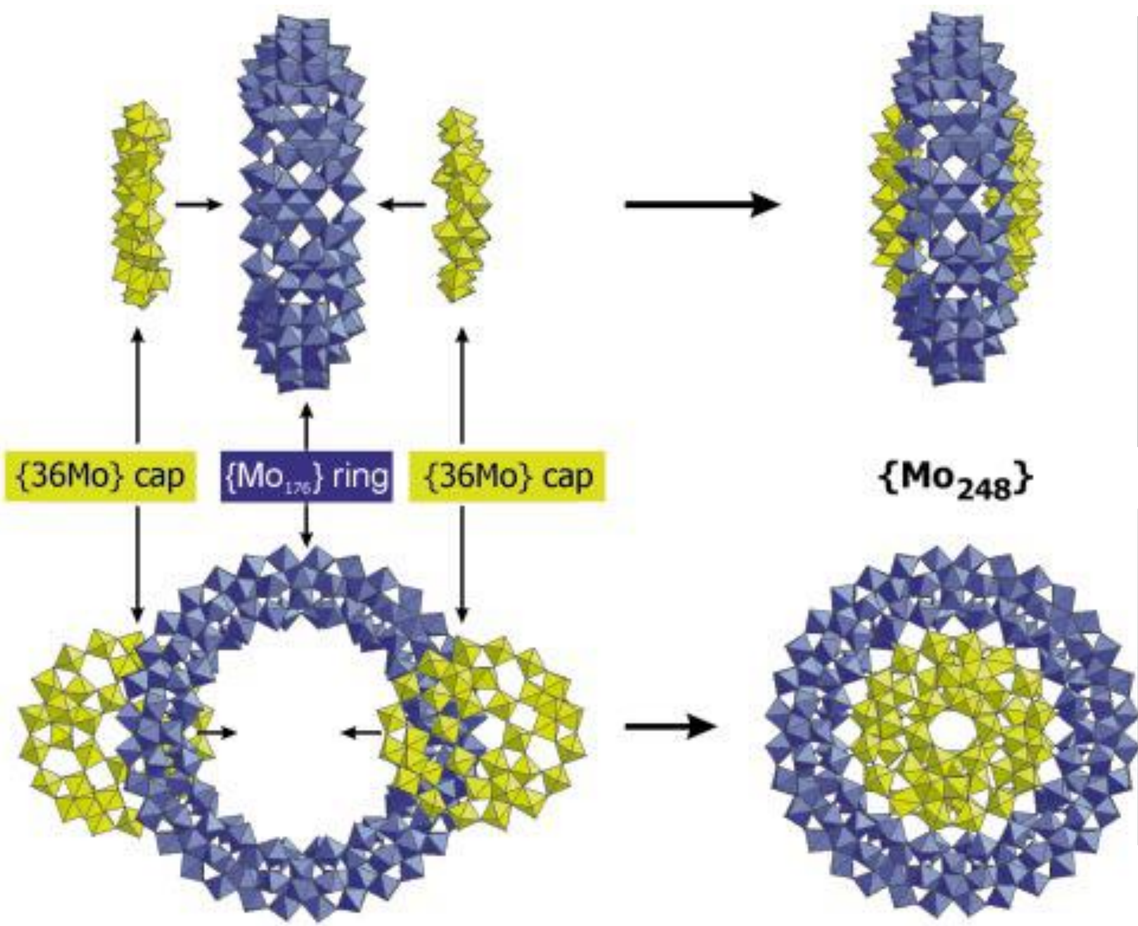
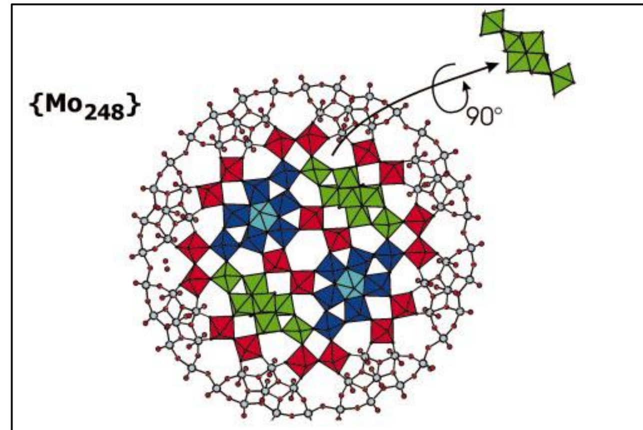
$\{Mo_{248}\} \equiv [\{Mo_2\}_{16}\{Mo_8\}_{16}\{Mo_1\}_{16}\{Mo_{36}\}_2]$





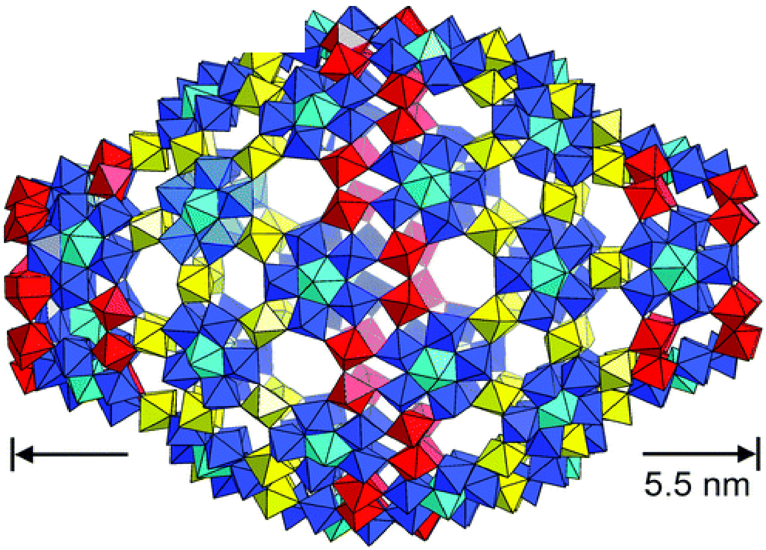
Closing of the upper and lower aperture of the initially formed $\{Mo^{176}\}$ by (formally) uncharged $\{Mo^{VI}_{12}Mo^{V}_{24}O_{96}(H_2O)_{24}\}$ **$\{Mo_{36}\}$** cluster. (highlighted hub-cap in polyhedral representation)

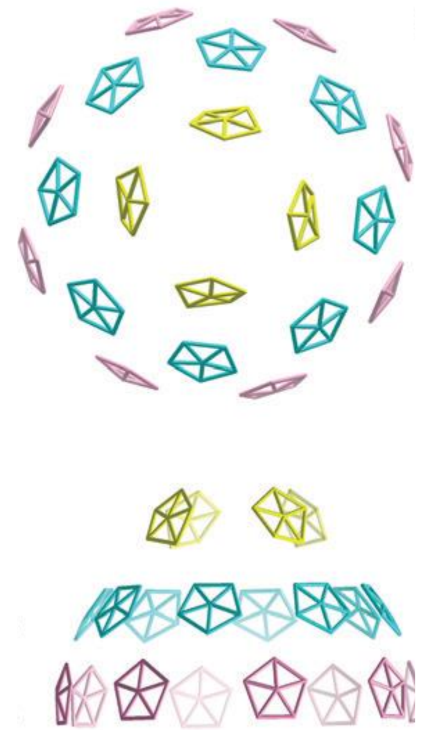
A. Müller and P. Gouzerh , *Chem. Soc. Rev.*, 2012, 41 , 7431-7463.
A. Müller, P. Kögerler, C. Kuhlmann, *Chem. Commun.*, 1999, 1347-1358.

Structural Types: The "Blue Lemon"

$\{Mo_{368}\}$-Lemon $[H_xMo_{368}O_{1032}(H_2O)_{240}(SO_4)_{48}]^{48-}$

Composed of three different types of building blocks: **64 $\{Mo_1\}$, 32 $\{Mo_2\}$, and 40 pentagonal $\{(Mo)Mo_5\}$ groups**





Comparable to the size of hemoglobin (external diameter ca. 6 nm).
It contains 368 metal (1880 non-hydrogen) atoms formed by the linking of 64 $\{Mo_1\}$, 32$\{Mo_2\}$, and 40 $\{(Mo)Mo_5\}$ type units (48 with sulfate ligands and 8 without)

A. Müller , E. Beckmann , H. Bögge , M. Schmidtmann and A. Dress , *Angew. Chem., Int. Ed.*, 2002, 41 , 1162-1167
B. W. M. Xuan , A. J. Surman , Q. Zheng , D. L. Long and L. Cronin , *Angew. Chem., Int. Ed.*, 2016, 55 , 12703-12707

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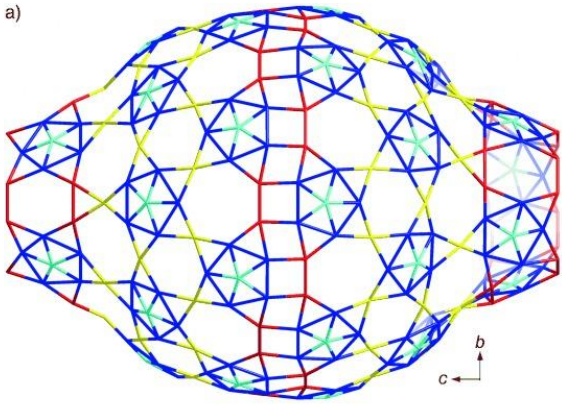
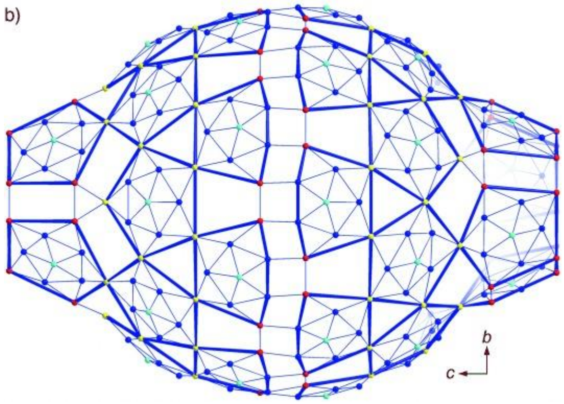


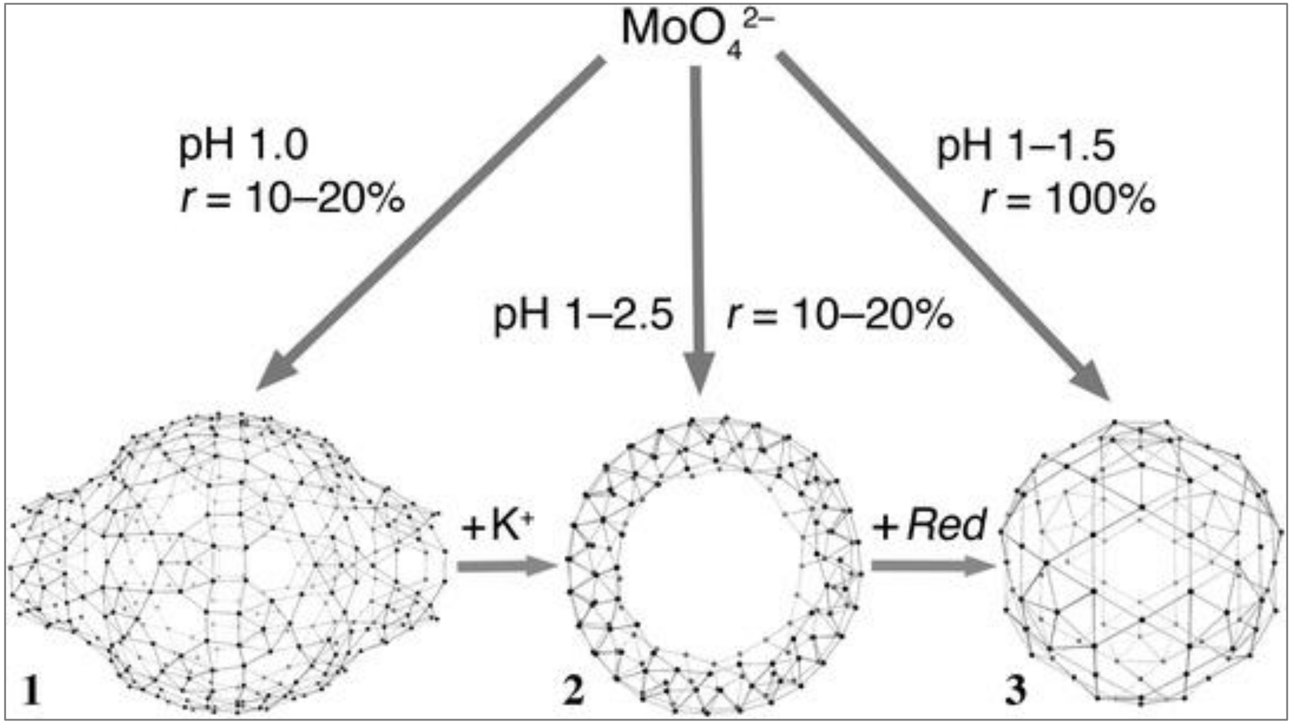


$\{Mo_{368}\}$ metal atom framework in wire-frame (a) and in ball and stick representation with $\{Mo_{11}\}$ and $\{Mo_{10}\}$ building blocks emphasized through thick lines (b; Color code: Building units $\{Mo_1\}$ yellow, $\{Mo_2\}$ red, $\{Mo(Mo_5)\}$ blue with blue-turquoise pentagonal bipyramids; O atoms small red spheres, S atoms gray spheres)).

$\{Mo_{368}\}$ consists of central spheroid-shaped fragment $\{Mo_{288}O_{784}(H_2O)_{192}(SO_4)_{32}\}$ and two capping units $\{Mo_{40}O_{124}(H_2O)_{24}(SO_4)_8\}$

A. Müller , E. Beckmann , H. Bögge , M. Schmidtmann and A. Dress , *Angew. Chem., Int. Ed.*, 2002, 41 , 1162-1167

The Key Reaction Parameters



Acidified aqueous solutions of sodium molybdate or ammonium eptamolybdate can be reduced by metal powders (Mo, Fe, Cu), hydrazine, hydroxylamine, sulphite, dithionite, thiosulphate, hypo-phosphorous acid, ascorbic acid, cysteine, $SnCl_2$, $FeCl_2$, and $MoCl_5$.

Schematic illustration of the self-assembled formation of the three distinct molybdenum blue structural types: lemon **1**, wheel **2** and sphere **3**. The key synthetic parameters (reduction degree *r* and solution pH) indicating the ideal conditions for the synthesis and interconversion between the three structural types are emphasized. Note that the synthesis of **1** requires the presence of sulfate ions.

B. Botar , A. Ellern and P. Kogerler , *Dalton Trans.*, 2012, **41** , 8951-8959