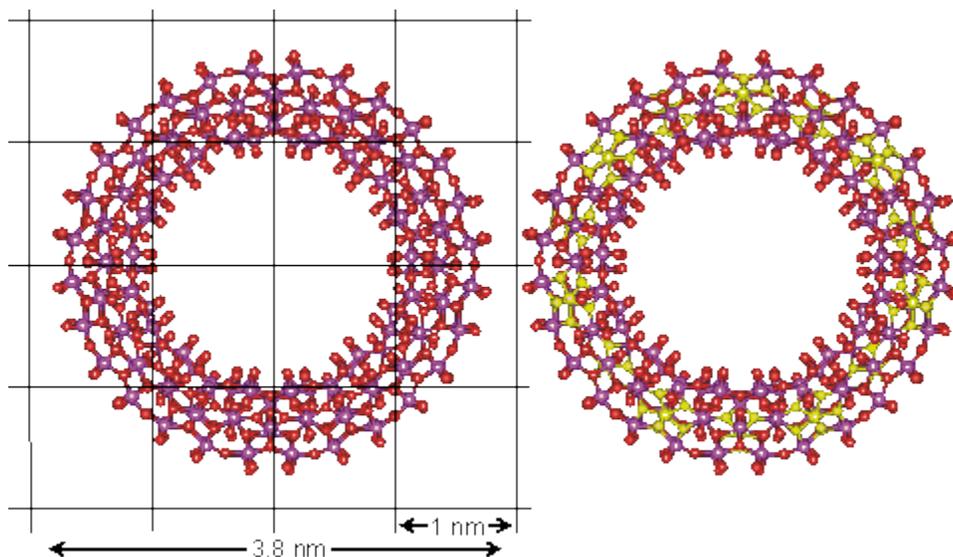


Molybdenum blue as polyoxomolybdate nanostructures

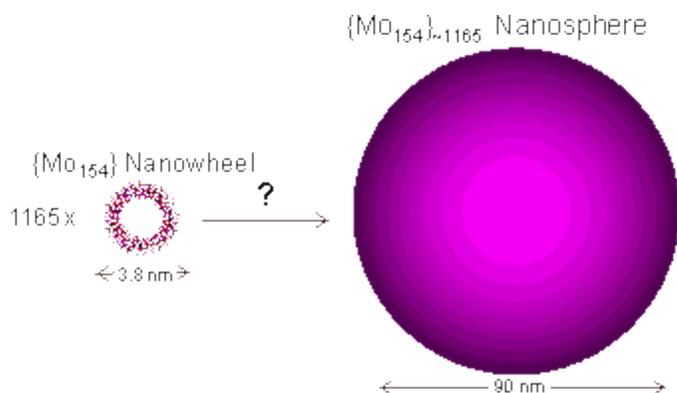
- ▼ [How does the {Mo₁₅₄} nanowheel hydrate?](#)
- ▼ [How do the 1165 hydrated {Mo₁₅₄} wheels form large spherical clusters?](#)

Molybdates in aqueous solution can form a vast variety of structures, due to the flexibility in the Mo-O-Mo links, the easy redox changes particularly involving Mo^V and Mo^{VI}, the different Mo coordination numbers possible, particularly 6 and 7, the strong hydration stabilization, and the formation of Mo=O chain termination [[1179](#)].

Of particular interest in aqueous solution are the self-assembling molybdate nanostructures; the Mo₁₃₂ nanocapsule, [mentioned elsewhere](#), and the 'molybdenum blue' {Mo₁₅₄} nanowheels ((Mo)Mo₅Mo₅O₃₃·(H₂O)₅]₁₄·(H₂O)_n) shown below and easily obtained from the well-defined, crystalline parent compound Na₁₅[Mo^{VI}₁₂₆Mo^V₂₈O₄₆₂H₁₄(H₂O)₇₀]_{0.5}[Mo^{VI}₁₂₄Mo^V₂₈O₄₅₇H₁₄(H₂O)₆₈]_{0.5}·400 H₂O [[1182](#)]. They are torus-shaped with highly hydrophilic surfaces.



This structure is notable as it has seven-fold symmetry. The surface to surface diameter of the torus is about 3.8 nm, with just under half taken up by the central cavity. There are fourteen pentagonal (Mo)Mo₅ groups (highlighted in yellow on the right), which alternate with seven on each side of the wheel. The interactive structure of this cluster is available ([Jmol](#)). The {Mo₁₅₄} nanowheels hydrate strongly on all surfaces to the surrounding solvent water, due to the 70 surface H₂O ligands and the large number of other surface oxygen atoms having high electron densities as the 14 (Mo)Mo₅Mo₅O₃₃ clusters each contain two delocalized 4d electrons, so also giving rise to the characteristic intense 'molybdenum blue' color [[1182](#)].

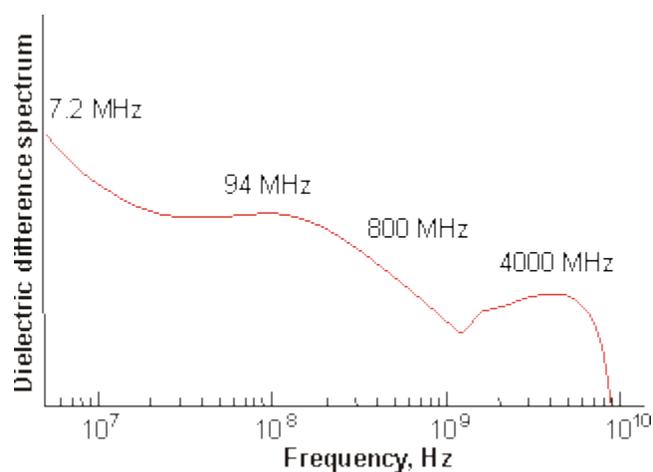


Over a period of days, the {Mo₁₅₄} nanowheels form very large, essentially monodisperse, blue spherical shells. These are perhaps the largest known self-assembling inorganic clusters. As the radius of gyration equals the hydrodynamic radius for these spheres they must consist of hollow spheres. Scanning electron microscope images and light scattering data show the radius and mass of the nanospheres is about 45.2 ± 1.4 nm with about 1165 {Mo₁₅₄} clusters on the nanosphere surface, leaving >50% extra space between the {Mo₁₅₄} nanowheels if evenly spread [1180]. Thus the {Mo₁₅₄} clusters may only contact each other through the interfacial water network.^a

This is a clear, if unusual, example of how a relatively small amount of interfacial water can organize very large volumes of liquid water. The question remains as to how 1165 such units with unusual seven-fold symmetry can form such highly ordered self-assembling structures. A putative model must not only show a rational final structure but also use a realizable route from the monomer to the complete cluster in agreement with the data.^b

How does the {Mo₁₅₄} nanowheel hydrate?

The clustering begins with the hydration of the {Mo₁₅₄} nanowheels. This has been investigated using conductance-corrected [dielectric difference spectra](#) of the freshly prepared 1.82 mM solution [1181]. In the spectrum (below) the wing of the intense absorption near 20 GHz and due to bulk water has been subtracted [1181].

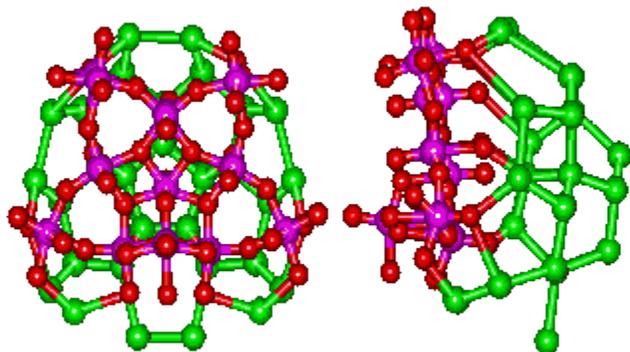


Nanowheel dielectric data

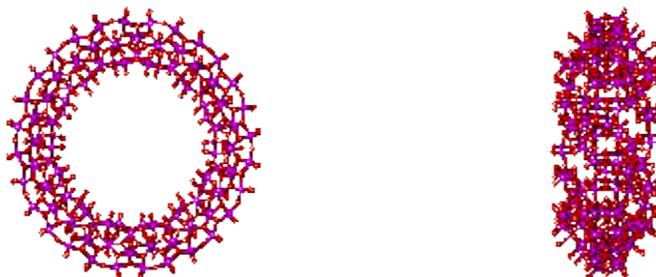
Water type	Assigned relaxation time, ns	Amplitude, H ₂ O	Amplitude, {Mo ₁₅₄ }
1	22 (7.2 MHz)	-	7.1
2	1.7 (94 MHz)	-	4.4
3	0.2 (800 MHz)	-	2.6
4	0.04 (4000 MHz)	-	2.8
Bulk	0.00822 (19400 MHz)	73.1	68.0

The amplitudes are proportional to the number density of the dipoles and the square of their dipole values in the bulk state. Due to their symmetry, the {Mo₁₅₄} nanowheels and larger vesicles do not possess a net dipole moment, thus, these amplitudes are due solely to the water molecules. Although the totality of the dielectric amplitude data has increased from 73.1 to 84.9, this may be accommodated simply by a 10% dipole increase of the bulk water, due to their increased polarization on clustering or, if spread out over all the water molecules, the dipole increase need be under 8%. Thus ~20% of the water in this 1.82 mM solution is associated with the {Mo₁₅₄} nanowheels, ~30% lies inside the spherical nanoshells (as calculated from their volume) and 50% is bulk water.

It is reasonable to assume that the hydration close to the surface of the 14 pentagonal (Mo)Mo₅ groups in the {Mo₁₅₄} nanowheels will be similar to that known to exist close to the 12 pentagonal (Mo)Mo₅ groups in the [{Mo₁₃₂} nanocapsule](#).



However, the {Mo₁₅₄} nanowheel (Mo)Mo₅ groups (Mo and O atoms shown magenta and red respectively) are surrounded by extra 'free' oxomolybdate which triple the number of potential anchor points from 5 to 15 (to H₂O, shown green) without straining the hydrogen bonding. Such an arrangement allows icosahedral clusters ([ES](#)) to be formed at each of the 14 such anchor points around the perimeter of the {Mo₁₅₄} nanowheel. The putative growth of this clustering is visualized below.

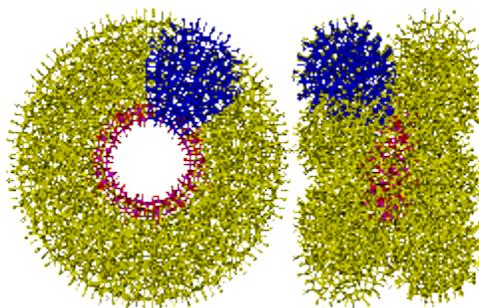


[Forward](#) [Backward](#)

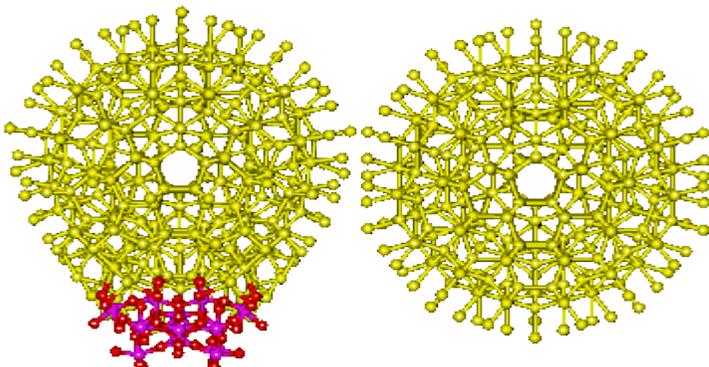
Only the oxygen atoms of the water network are shown **yellow** above.

The hydration of the $\{\text{Mo}_{154}\}$ nanowheel is outlined opposite (press the **Forward** button) indicating the layers of hydration, although they are not thought to build up exactly as shown.

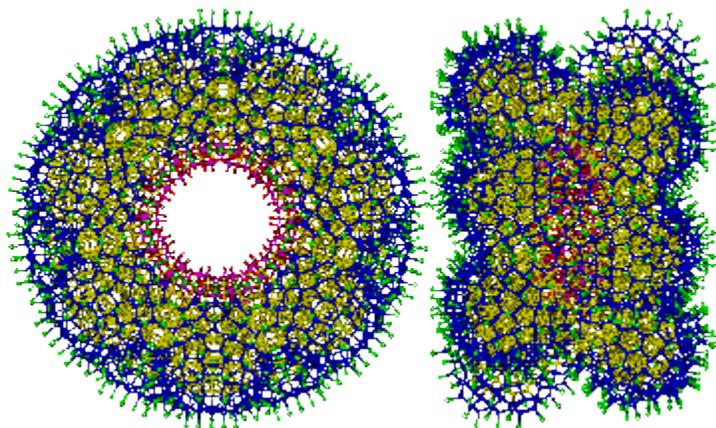
Below is shown (**blue**) the hydration associated with one of the 14 $(\text{Mo})\text{Mo}_5$ anchor points.



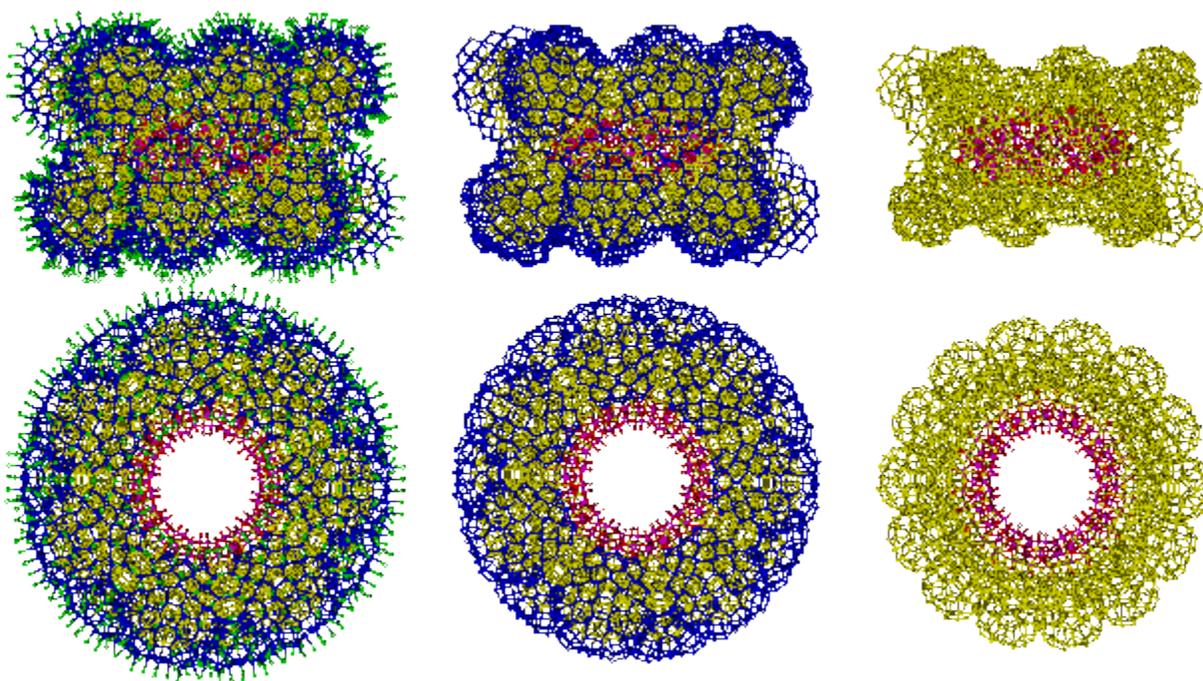
Shown below is the $(\text{H}_2\text{O})_{376}$ water cluster arrangement held by each one of the 14 $(\text{Mo})\text{Mo}_5$ anchor points, compared with the arrangement of the $(\text{H}_2\text{O})_{400}$ water cluster in the icosahedral water cluster (**ES**); only the O-atoms of water are shown, **yellow**.



Three layers of hydration around the $\{\text{Mo}_{154}\}$ nanowheel are indicated below in green, blue and yellow. There are 14 sites with clear potential for binding cations such as Na^+ , indicated below by mousing over the image. These sites lie on the inner surface of the nanowheels rather than their highly hydrated outer surface, where they would necessarily disrupt the hydrogen bonding.



If the arrangement of water around $\{\text{Mo}_{154}\}$ nanowheels is similar to the [icosahedral clustering established earlier](#), then the hydration falls into three distinct layers.



Cartoon showing the hydration assignment involving icosahedral clustering around each $(\text{Mo})\text{Mo}_5$ center, ignoring the hydration space in the middle of the torus. There are 980 loosely-held ([hydrogen-bonded](#)), H_2O (O-atoms shown green above) either singly-linked or doubly-linked on the outside of the cluster. Underneath lies 1778 still triply-linked (after removal of the loosely held water) then singly linked (after removal of the triply-linked) H_2O (both shown blue). Closest to the nanowheel is an inner layer of 2506 still triply- and tetra-linked (after removal of the outer two layers) H_2O (shown yellow).

The numbers of molecules in the hydration layers fit neatly with the results from the dielectric absorption spectra:

Nanowheel dielectric water data				
Water type	Relaxation time, ns	Amplitude	Experimental, % H ₂ O (H ₂ O/Mo ₁₅₄)	Calculated from model, % H ₂ O (H ₂ O/Mo ₁₅₄)
1	22	7.1	8.3 (2505)	8.4 (2506)
2	1.7	4.4	5.2 (1552)	5.9 (1778)
3	0.2	2.6	3.1 (917)	2.7 (798)
4	0.04	2.8	3.3 (988)	3.3 (980)
Bulk	0.00822	68	80.1	79.8

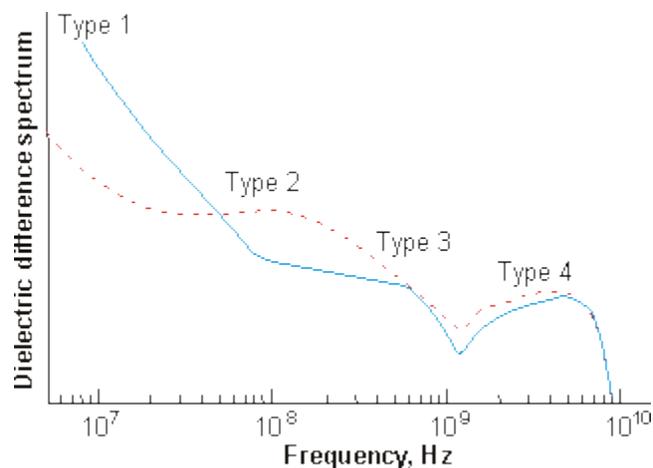
where type 1 water constitutes the inner water shell (shown yellow above), type 2 water constitutes the middle water shell (shown blue above), type 3 water constitutes the water within central cavity (calculated using its volume and the normal density of water) and type 4 water constitutes the outer water shell (shown green above). There are about 29950 moles of water per mole of {Mo₁₅₄} nanowheel present of which ~20% is associated; representing 5962 molecules of H₂O. The model, which has been developed independent of this dielectric data, indicates 6062 molecules of H₂O (<2% error) with a remarkably good fit with the occupancy of the layers considering the precision of the dielectric data. The type 3 water is the most error-prone of all the assignments as the extent of the central space within the torus is poorly bounded top and bottom but here estimated from the content of a cylindrical volume bounded by the strong type 1 and type 2 water clustering only. Although these assignments have been chosen as a fit for the experimental data, the water cluster model is established [55] and fits the closely related hydrated [polyoxomolybdate nanocapsule](#) as examined by X-ray diffraction [547].

How do the 1165 hydrated {Mo₁₅₄} wheels form large spherical clusters?

The 1165 polyoxomolybdate {Mo₁₅₄} nanowheels distributed on the surface of the 90 nm spherical cluster [1180] must be separated from each other by several hydration layers (on average) as the center-to-center distance between two adjacent nanowheels would be about 5.0 nm using hexagonal, or 4.7 nm using square, close-packing whereas the surface-surface diameter of an individual nanowheel is only 3.8 nm [1180]. Even if a surface could be formed from the nanowheels utilizing just three neighbors for each nanowheel (for example, not close-packed but with similar topology to the fullerenes, [see later](#)), these would have to be 4.1 nm apart at their extremities, still necessitating the utilization of interfacial water molecules. Additionally such a structure, based on three-fold symmetry would not fit with their seven-fold symmetry. It has been suggested that the driving force for the assembly of these structures is a delicate balance between short-range attractive forces (van der Waals forces and hydrogen-bonding forces) and repulsive electrostatic interactions between adjacent anion clusters [1180b]. Due to the extended time required for forming these clusters and the changes in dielectric spectra and small angle X-ray scattering (SAXS) [1180a] on solution ageing, it is clear that the clustering must take place in stages.

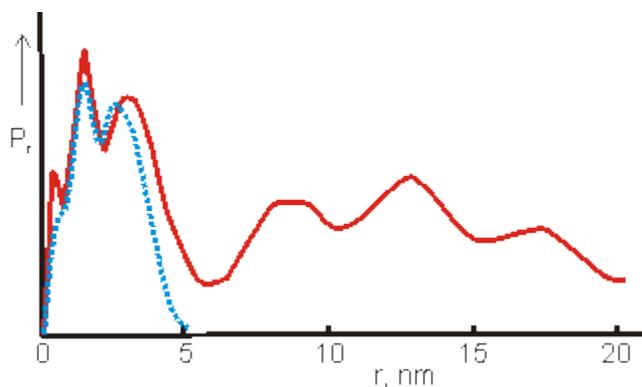
There are four experimental datasets that the hydration and clustering of the {Mo₁₅₄} nanowheels has to conform; dielectric spectroscopy [1181], small angle X-ray diffraction [1180a], light scattering [1180b] and scanning electron microscopy [1180]. In addition, the proposal cluster growth must be soundly based.

The conductance-corrected dielectric difference spectra of the aged 1.82 mM solution, on nanowheel vesicle formation, is shown below right (blue line) [1181] and compared with that of the fresh solution (dashed red line) discussed above.



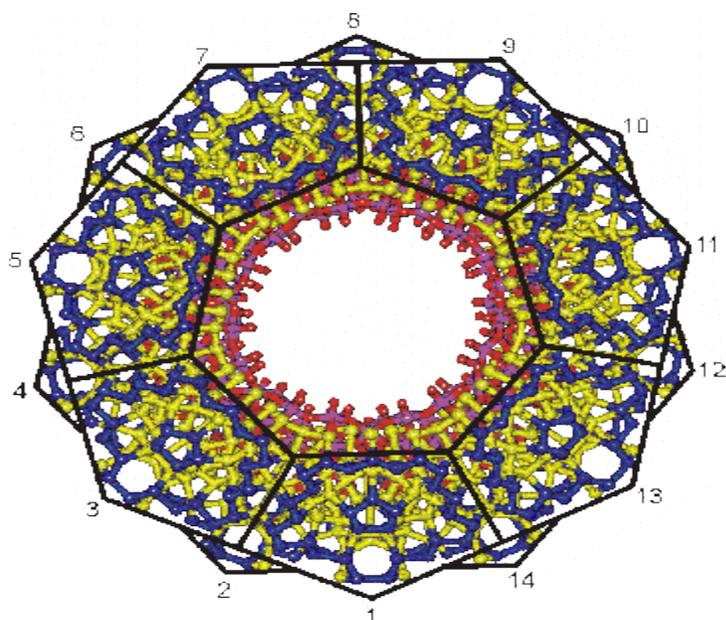
Changes in dielectric spectra on aging		
Water	Relaxation time	Amplitude change
Type 1	Stays at ~22 ns	Almost doubles
Type 2	Stays at ~1.7 ns	Reduces by more than 50%
Type 3	Increases from 0.2 ns to 0.35 ns	Reduces to 60%
Type 4	Stays at ~ 0.04 ns	Stays about the same
Bulk	Stays at ~ 0.00822 ns	Stays about the same

The conclusions that can be drawn from this dielectric data is that more type 1 water is strongly bound, less type 2 water is found and is bound less-strongly, less type 3 water is found in the cavities but it is more strongly bound and the type 4 surface-bound water is unaffected as is the bulk water.



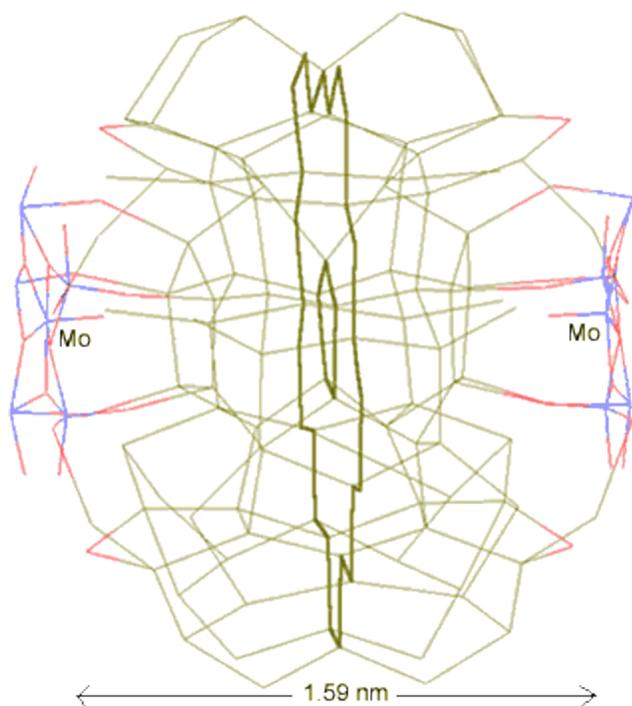
Shown opposite is the distance distribution function from small-angle X-ray scattering (SAXS) data obtained from a freshly prepared solution of the $\{Mo_{154}\}$ nanowheels (blue dotted) and from the same solution after two days (red line) [1180] showing the formation of oligomers.

The first stage in the vesicle formation from $\{\text{Mo}_{154}\}$ nanowheels must be the formation of dimers utilizing a similar water clustering arrangement to that proposed above for monomer hydration and found in supercooled water ([ES](#)) and the hydrated [polyoxomolybdate nanocapsule](#) [547].



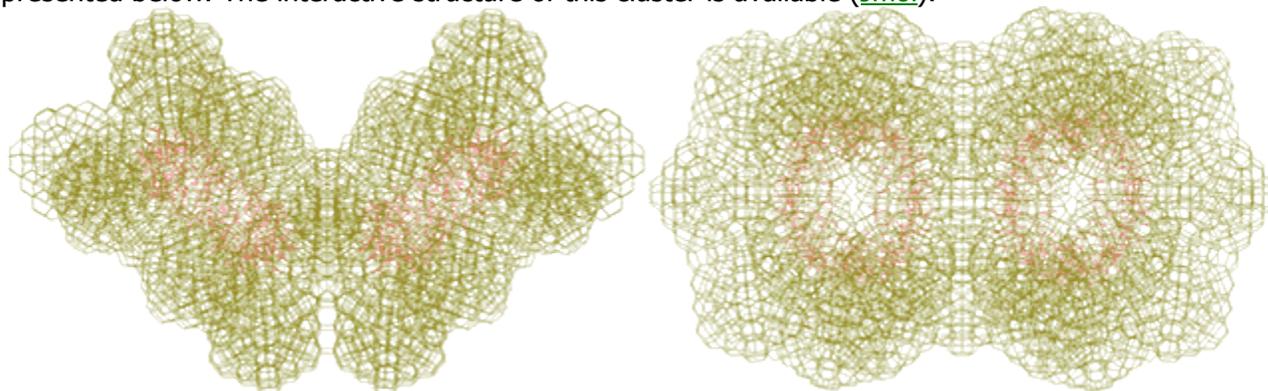
The cartoon right shows the putative hydration linking faces on the $\{\text{Mo}_{154}\}$ nanowheel based on the 14 $[(\text{Mo})\text{Mo}_5\text{Mo}_5\text{O}_{33}(\text{H}_2\text{O})_5]$ anchor points.

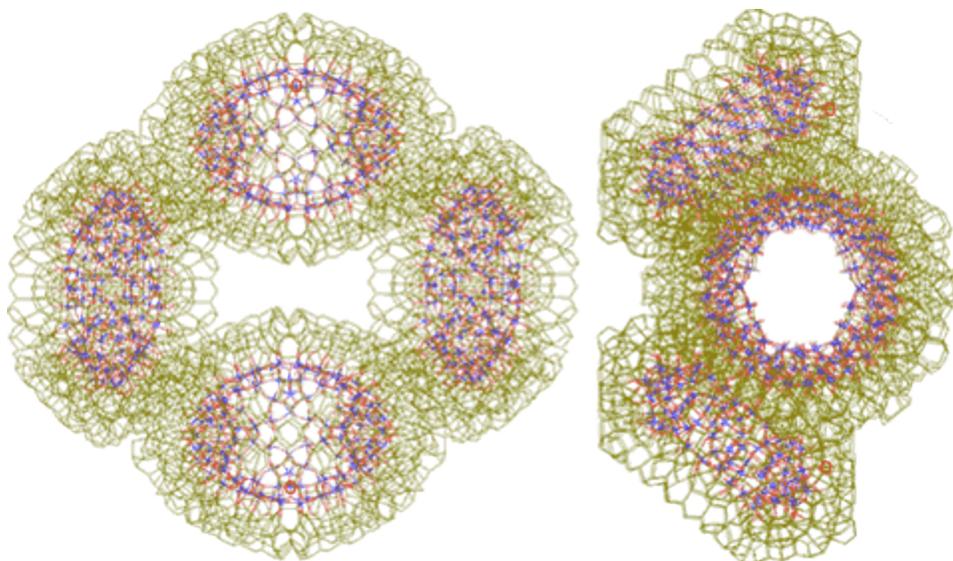
Hydrating water is colored **yellow** with the linking faces colored **blue** (only the O-atoms of water are shown). Every hydrated $\{\text{Mo}_{154}\}$ nanowheel has 14 possible linking surfaces based upon the pentagonal anchors shown [above](#). In this cartoon all icosahedral clusters have been truncated at their putative linking surfaces. In the hydrated oligomers unused linking surfaces would be expected to retain their icosahedral clustering, with somewhat enhanced hydrogen bonding by the more extensive oxomolybdate surfaces. During formation of the 90 nm spherical supercluster, described below, hydrated $\{\text{Mo}_{154}\}$ nanowheels develop from [tetramers](#). In each tetramer, two nanowheels are linked by their 1, 6 and 10 faces, one by its 1, 4 and 7 faces and the fourth by its 1, 9 and 12 faces. An [extra linkage](#) to either, but not both, these latter two nanowheels may be formed through their 11 or 5 faces respectively.



Thus, two $\{Mo_{154}\}$ nanowheels may link through a water network involving two pentagonal boxes (one associated with each $[(Mo)Mo_5Mo_5O_{33} \cdot (H_2O)_5]$ anchor point), with the topology shown left. The water O-atoms are colored green with the H-atoms left out for clarity. The central Mo---Mo distance between clusters is about 1.59 nm.

The complete hydrated dimers with their complete icosahedral clusters on the unlinked surfaces are presented below. The interactive structure of this cluster is available ([Jmol](#)).

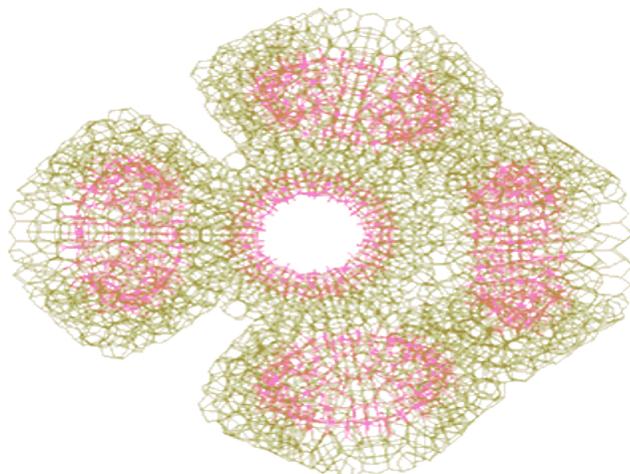




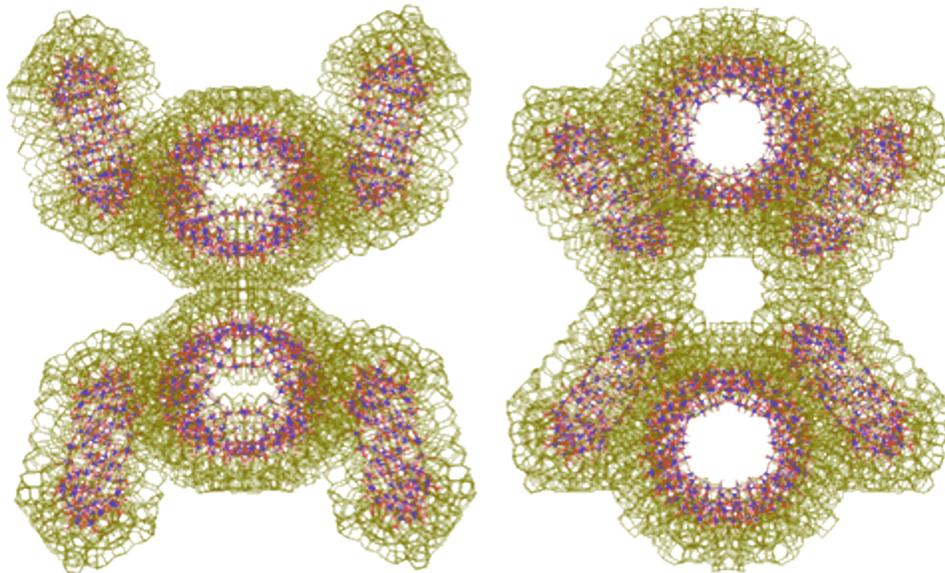
Two $\{Mo_{154}\}_2$ dimers can form a tetramer $\{Mo_{154}\}_4$, stabilized by four of the hydrogen-bonded linking water clusters.

Such tetramers have been previously suggested as the dominating cluster from SAXS studies [[1180](#)].

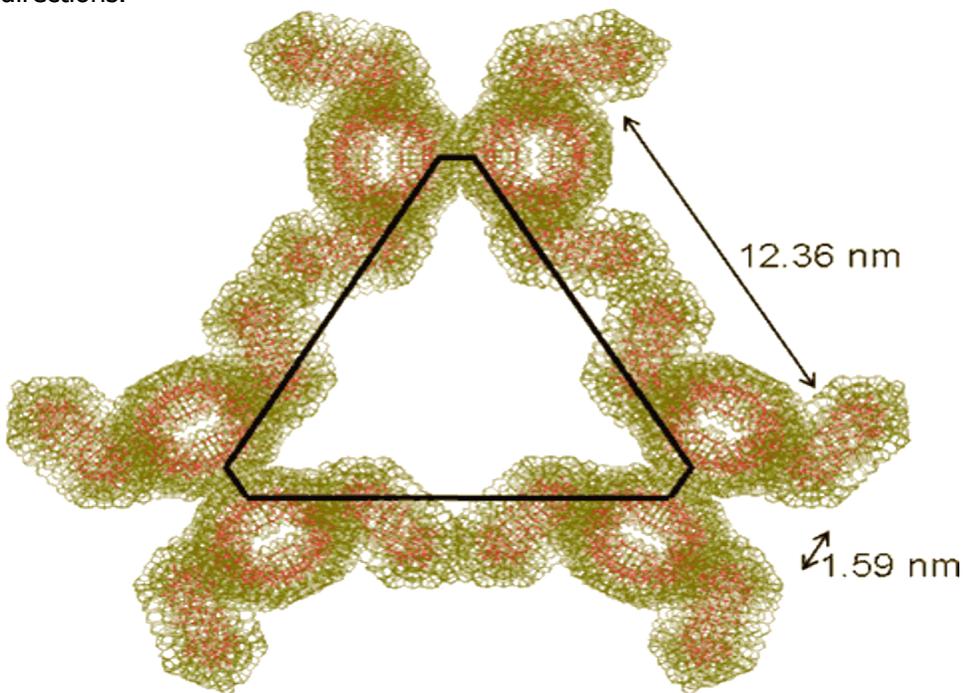
The interactive structure of this cluster is available ([Jmol](#))



Each tetramer can add one further $\{Mo_{154}\}$ nanowheel to one of two alternate positions to form a pentamer (these positions are shown by the red circles in the figure above and the complete pentamer is shown left) as [indicated above](#). This additional $\{Mo_{154}\}$ nanowheel may be added at any stage in the further clustering towards the nanoshell formation, but space exists for no more than one $\{Mo_{154}\}$ nanowheel to be added to close the structure of each tetramer, so being stabilized by neighboring icosahedral water clustering.

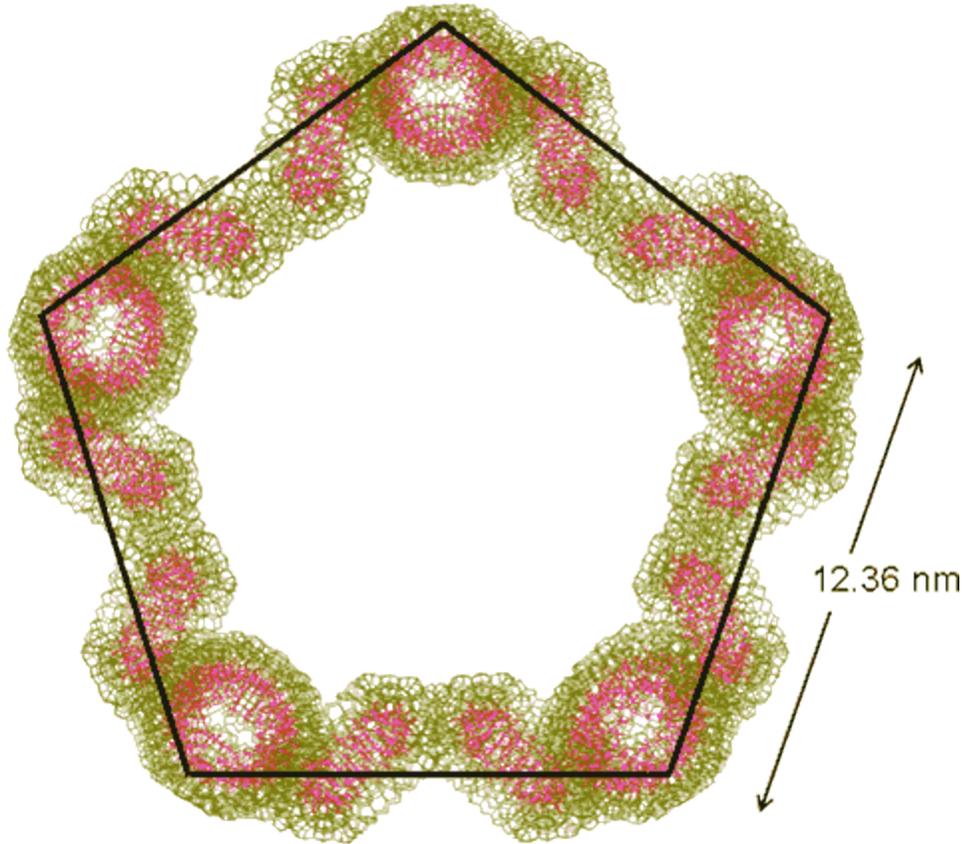


Two tetramers (or pentamers) can further join through two further linking water clusters to form octamers ($\{\text{Mo}_{154}\}_4\}_2$ (or decamers). See right for nanowheel octamers, as viewed from different directions.



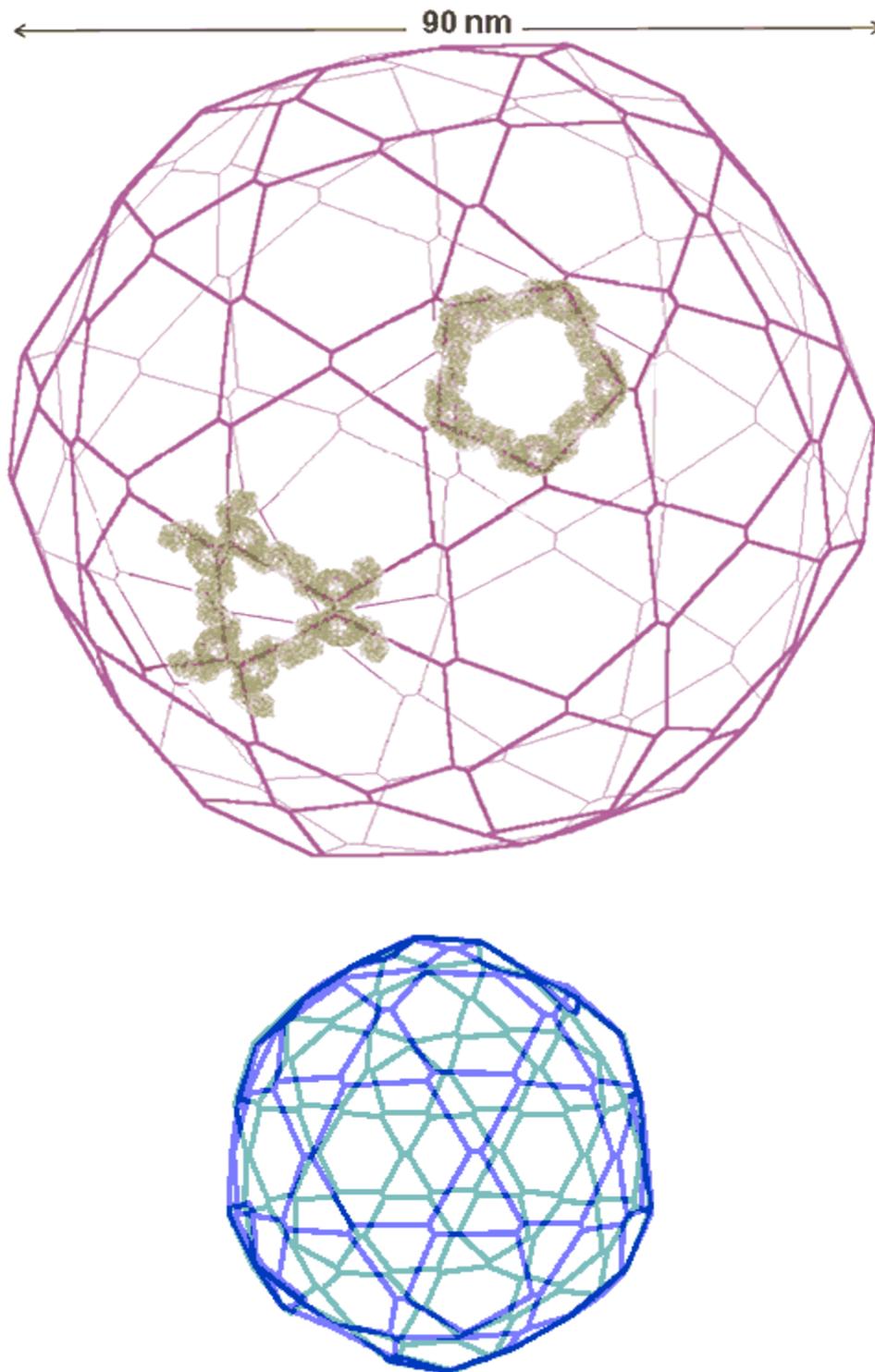
Three of the octamers shown above can cluster into a distorted $[(\{\text{Mo}_{154}\}_4\}_2)_3$ hexagon as shown left. These distorted hexagons thus contain 24 $\{\text{Mo}_{154}\}$ nanowheels held together by 33 linking water clusters. As shown later, these octamers form the surface of the nanoshell supercluster.

The distance between tetrameric clusters (12.36 nm) and the diameter of the distorted hexagon (mouse image to view) have been found close to the major peak in the [SAXS experimental data](#) (12.7 nm) [1180].



Five $\{\text{Mo}_{154}\}_4$ tetramers may also cluster to form a regular pentagon (with 20 $\{\text{Mo}_{154}\}$ clusters, shown opposite) and six $\{\text{Mo}_{154}\}_4$ tetramers may cluster to form a regular hexagon ring (with 24 $\{\text{Mo}_{154}\}$ clusters). Such rings are formed from singly-linked tetramers but stabilized by the ring closure. They are also formed consequent upon the clustering of the distorted hexagons (above).

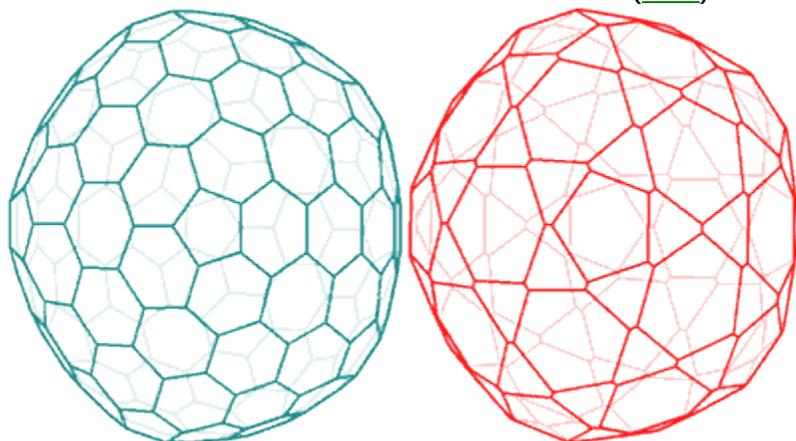
It is proposed that the final assembly of the nanosphere is made up from the distorted hexagons in such a way that undistorted pentagons and hexagons are also formed (see below).



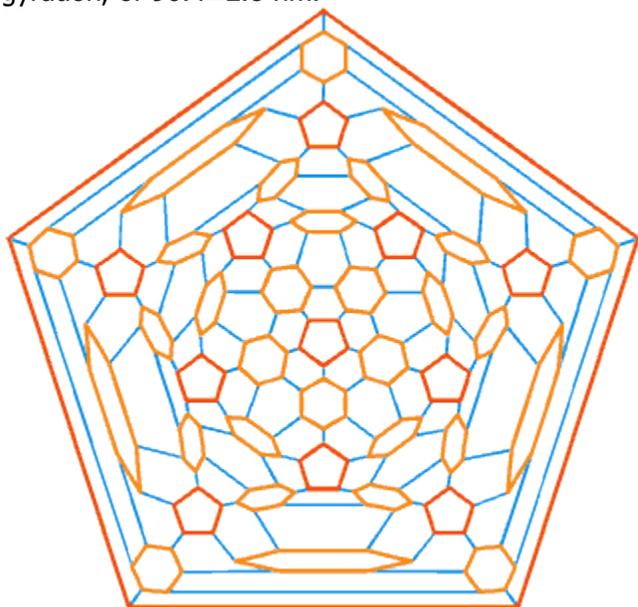
Each vertex in this nanoshell is the Mo atom at the water hydrogen-bonded linkage of a tetramer. The 90 nm nanosphere has 240 vertices requiring a minimum of 960 $\{\text{Mo}_{154}\}$ nanowheels. Without altering the shell diameter, each of the 240 $\{\text{Mo}_{154}\}_4$ tetramers may add a further $\{\text{Mo}_{154}\}$

nanowheel to give a maximum content of 1200 $\{\text{Mo}_{154}\}$ nanowheels, if completely assembled from $\{\text{Mo}_{154}\}_5$ pentamers.

The interactive structure of this cluster is available ([Jmol](#)).

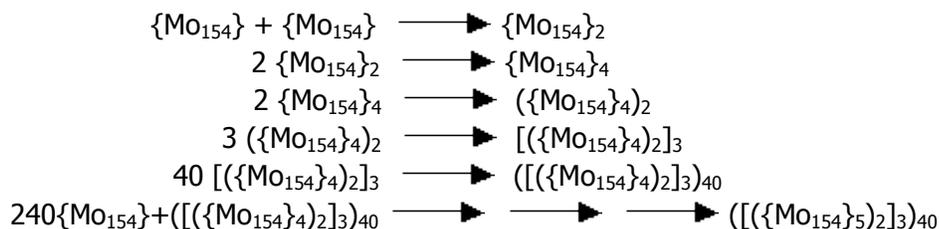


The spherical nanoshell has the same topology as a fullerene, C_{240} . The C_{240} is only 1.44 nm in diameter whereas the 'model' $\{\text{Mo}_{154}\}$ has a surface-surface diameter of ~ 90.6 nm. This may be compared with the diameter determined experimentally by light scattering, from the radius of gyration, of 90.4 ± 2.8 nm.



The diagram opposite is connectivity map for the proposed spherical nanoshell. Easily seen are the 12 pentamers (red), 30 symmetric hexamers (orange) and 80 distorted hexamers that make up the spherical shell. The shells can either be thought of as formed from 12 regular pentagons (that is, $12 \times 20 \sim 24 \{\text{Mo}_{154}\}$) plus 30 regular hexagons (that is, $30 \times 24 \sim 30 \{\text{Mo}_{154}\}$) linked together, or as formed from 80 distorted hexagons with shared edges (that is, $80/2 \times 24 \sim 30 \{\text{Mo}_{154}\}$).

The route to the supercluster involves a sequence of associations with increasing proportion of linkages providing the enthalpic gain to overcome the decreasing entropy of formation [[1183](#)]:



Links/{Mo₁₅₄}

0.5
1.0
1.25
1.375
1.5
1.4

In this way the spherical supercluster $([(\{\text{Mo}_{154}\}_{4\sim 5})_2]_3)_{40}$ is built up with an increasing number of links per $\{\text{Mo}_{154}\}$ nanowheel used, which overcomes the reduced entropy. The final $\{\text{Mo}_{154}\}$ content is 960-1200 which agrees with the average of 1165 that has been found experimentally. Once the 90 nm spherical superclusters are formed they will retain weak linkage positions on the outside that can enable their aggregation, as seen in the scanning electron microscope images [1180].

Footnotes

^a It is not thought simply to be a nanobubble (nanocavity, for example, see [1172]), as the $\{\text{Mo}_{154}\}$ nanowheel is not amphiphilic, the size of the nanosphere is exact and the pressure inside may otherwise be unstably high at 3.2 MPa, if the [Laplace equation](#) holds. If [nanobubbles](#) (that is, nanocavities) were involved, it would be expected that the amount of nanoparticle involved would be independent of the size of the [nanobubbles](#) (as the nanoparticles congregate favorably at the gas/liquid interface), which is not the case here. Also there would be expected to be a need for an amphiphilic solute [1172].

^b A useful and interesting review of this area has been written which presents a different hypothesis to the one described here [1223].

Source: <http://www1.lsbu.ac.uk/water/giant.html>