The Potential of Pentagonal Building Blocks: From Giant Ring-shaped to Spherical Polyoxometalate Clusters

Leroy Cronin

The deliberate construction of multifunctional compounds using the most elegant synthetic strategy possible, the one pot reaction, is one of the most challenging problems in contemporary chemistry.[1] Conceptually it is more straightforward to consider the synthesis in terms of successive steps of reaction and isolation, following the logic of retrosynthesis.[2] However it is obvious that the chances of success (synthesising such molecules on a reasonable time-scale and in good yield) using this approach decrease very rapidly indeed as the number of steps in the synthesis increase. A potentially powerful alternative to such an approach can be gained by observing the way in which nature overcomes this problem – by the exploitation of weak interactions and symmetrical complementarity in the assembly of massive architectures such as DNA, Viruses and proteins.[3] Nature, by carefully controlling the properties of the building blocks, is able to facilitate the 'self-assembly' as well as stepwise growth of such systems and thereby bypass the problems associated with the pure stepwise synthesis. The result is truly amazing, giving massive molecules with incredible functionality and molecules with the ability to replicate – the molecules of life.[4]

This chapter describes the one-pot synthesis of ring-shaped and spherical polyoxometalate clusters, based on a set of structurally conserved building blocks, will be described. These building blocks are suggested to have intrinsic properties (high and variable charge and flexible ligand coordination modes) that facilitate the self assembly of clusters containing many thousands of atoms in solution. Through this comparison one can draw parallels between the properties of polyoxometalate building blocks and those utilised by nature. Therefore, in this respect, the use of *pentagonal-type building groups,* with different symmetries, play a key role in the synthesis of these systems. This can be taken further by considering that edge-sharing (condensed) pentagons cannot be used to tile an infinite plane,[5-7] whereas exactly 12 pentagons are required, in connection with well-defined sets of hexagons, to construct spherical systems such as that observed in the truncated icosahedron – the most spherical Archimedean solid –, in polyhedral viruses, or in the geodesic Fuller domes.[8] Therefore the use of pentagonal building blocks is absolutely essential in *chemistry*, if one is able to produce curved species – the paradigm of which is C_{60}.[6]

From a synthetic point-of-view, one basic principle (the acidification of a solution of molybdate and its subsequent reduction) has been shown to lead to two classes of compounds that are built from a related set of molybdenum-based building blocks.[9-10] These are; (a) $\{Mo_{132}\}$-based *spherical icosahedral inorganic superfullerenes or Keplerates* and (b) $\{Mo_{154}\}$ / $\{Mo_{176}\}$-based *ring-shaped, mixed-valence species with nanosized cavities*. Although the mechanisms for the construction of such clusters are not understood, one can consider the consequences of the incorporation of 5-fold directing building units as a factor in the synthesis of both types of geometrically closed (ring and spherical) clusters.[11]

Furthermore, a structural decomposition of both types of these molybdenum-oxide based giant clusters has revealed that both types of cluster consist of multiple $\{Mo_{11}\}$ units where $\{Mo_{11}\} \equiv \{(Mo)^0(Mo_5)^I(Mo_5)^{II}\}$ building block and the central (directing) pentagonal unit is, MoO_7 bipyramid ($\equiv (Mo)^0$) in accordance with Fig. 5.1.[12] It is remarkable ,therefore, from a structural point-of-view that, both types of species are based on building blocks which have almost the same stoichiometry (the $\{Mo_{11}\}$ with C_S symmetry has one less oxygen atom) and a central directing pentagonal bipyramid, Fig. 5.2.[12] Overall, these processes can be described as based on variably linkable polyoxometalate building groups (face sharing, corner sharing, etc) "present" in solution either as existing or virtual fragments as which become available on demand from a kind of 'library' depending on the boundary conditions, i.e. on which other species are present as templates etc.
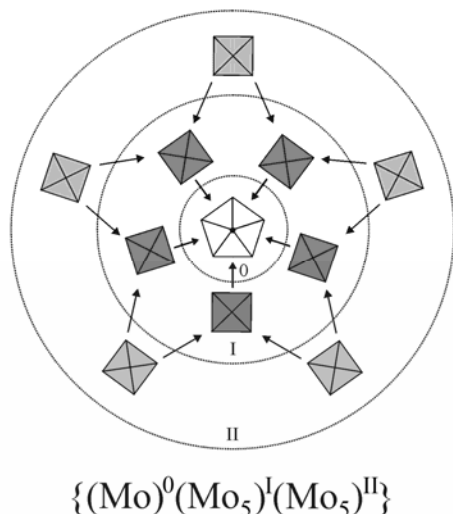

$$\{(Mo)^0(Mo_5)^I(Mo_5)^{II}\}$$

Figure 5.1. Schematic representation of the $\{Mo_{11}\} \equiv \{(Mo)^0(Mo_5)^I(Mo_5)^{II}\}$ building group with its central part, a pentagonal-bipyramidal MoO_7 unit, having a directing function. Five MoO_6 octahedra of the $(Mo_5)^I$ type are condensed to the equatorial plane of this central MoO_7 unit, sharing edges, while the next five MoO_6 octahedra of the $(Mo_5)^{II}$ type share corners with the former octahedra.

To rationalise further the reasons for the differences between the two sets of clusters and their constituent $\{Mo_{11}\}$ building blocks, one should consider the degree of reduction of the Mo atoms which comprise the $\{Mo_{11}\}$ unit. The degree of reduction of the $\{Mo_{11}\}$ unit is critical in determining the symmetry of the $\{Mo_{11}\}$ building block, and therefore the composition of the cluster obtained, for instance in *spherical systems* such as the $\{Mo_{11}\}_{12}$ cluster the Mo atoms of the peripheral $(Mo_5)^{II}$ shell are equivalent, i.e. they are all of the Mo^V type, and for *lower symmetrical wheel-type systems* such as the $\{Mo_{11}\}_n$ (n = 14, 16) species the relevant five Mo atoms are not equivalent (with an average oxidation number higher than V). The crucial aspect that decides whether the $\{Mo_{11}\}$ groups will form spherical $\{Mo_{11}\}_{12}$-type cluster ($\{Mo_{132}\}$) with fivefold local symmetry or a ring shaped cluster lies in degree of the reduction of the $\{Mo_{11}\}$ unit. Regular $\{Mo_{11}\}$ groups of C_5 symmetry require five equivalent $(Mo^V)^{II}$-type MoO_6 octahedra bound to the $\{(Mo)^0(Mo_5)^I\}$ pentagons. This is achieved only in the presence of a (comparably strong) reducing agent in the appropriate concentration which can reduce all of these five peripheral $(Mo)^{II}$-type atoms to Mo^V. It has been observed that if the related reduction potential is not met (while working at relatively high H^+ concentrations correspondingly to pH $\approx$ 1-2 and not pH $\approx$ 4 with the formation of the $\{Mo_{11}\}_{12}$ system), the five peripheral Mo centres are only partially reduced, with the consequence that they are no longer equivalent and the whole group has no longer fivefold symmetry. In this case other types of $\{Mo_{11}\}_n$ species such as the ring-shaped clusters are formed, for instance when n = 14, giving a $\{Mo_{154}\} = \{Mo_{11}\}_{14}$-type cluster.[9] Here the $\{Mo_{11}\}$ groups differ from those present in the aforementioned $\{Mo_{11}\}_{12}$-type superfullerene in the sense that one of the peripheral MoO_6 octahedra is positioned in such a way that the $\{Mo_{11}\}$ group – as mentioned above – correspondingly shows only C_s symmetry.

In the case of polyoxomolybdates with pentagonal groups of the form $\{(Mo)Mo_5\}$ $\{(Mo)^0(Mo_5)^I\}$ [which consist of a central bipyramidal MoO_7 unit $((Mo)^0)$ sharing edges with 5 MoO_6 octahedra $((Mo_5)^I$ type], it should be realized that these groups are the starting point for quite a number of spherical-type clusters.[13] However, to consider the construction of the spherical clusters represented in Fig. 5.3. it is more informative to adopt a slightly different building block notation. Empirically, as stated earlier, the spherical $\{Mo_{132}\}$-based cluster can be reduced to twelve $\{Mo_{11}\}$ groups. But the $\{Mo_{132}\}$ cluster comprises 12 $\{(Mo)Mo_5\}$ pentagonal units and 30 $\{Mo^V_2O_4\}^{2+}$ 'linker' units. For these linkers to be present in the reaction medium it has been shown that the presence of bidentate ligands is required.
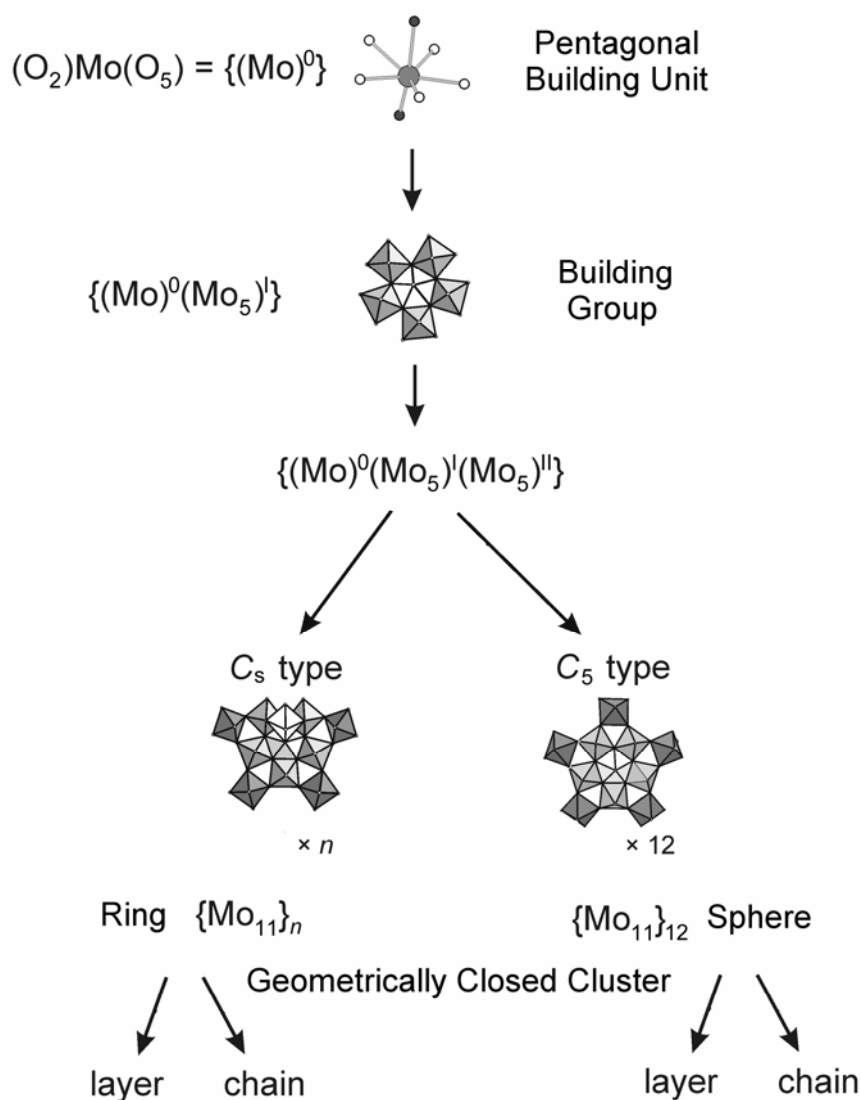

Figure 5.2. This scheme shows the construction principle of systems based on the $\{Mo_{11}\}$ building groups corresponding to Figure 5.1.

Therefore, the combination of a solution of reduced molybdate and acetate results in an icosahedral molecular system with the stoichiometry $[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]^{42-}$. $\{Mo_{132}\}$ $\overset{\sim}{\vphantom{x}}$ $\{Mo_{11}\}_{12}$ (Fig. 5.3) [6]. In this cluster the central Mo positions of the $\{(Mo)^0(Mo_5)^I\}$ pentagons define the 12 corners, and the $\{Mo^V_2O_4\}^{2+}$ groups the 30 edges, of an icosahedron, a situation which is in agreement with Euler's well-known formula. (This corresponds to the formulation $[\{(Mo)Mo_5O_{21}(H_2O)_6\}_{12}\{Mo^V_2O_4(CH_3COO)\}_{30}]^{42-}$.)
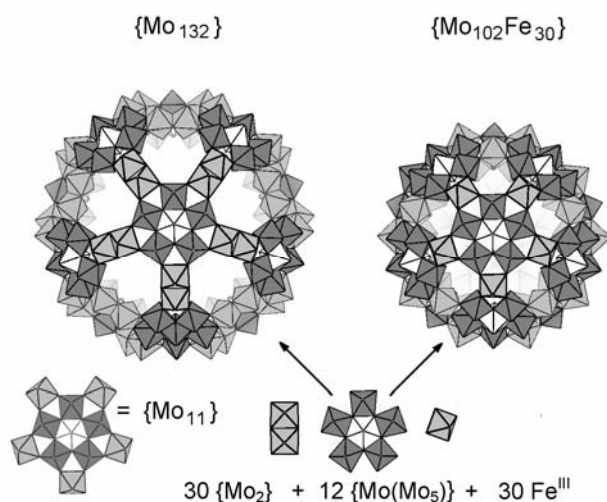

Figure 5.3. Comparison of the polyhedral representations of the $\{Mo_{11}\}_{12}$ (left-hand-side) and $\{(Mo)^0(Mo_5)^I(Fe_{5/2})^{II}\}_{12}$ (right-hand-side) spherical clusters along with along with a representation (below each cluster) of the repeating units present in each cluster. The pentagonal centres of the $\{Mo(Mo_5)\}$ are shown in white, the $\{Mo_2\}$ groups and Fe-based octahedra are light grey polyhedra and the remaining (Mo_5) of the $\{Mo(Mo_5)\}$ unit are dark grey polyhedra. A representation of the $\{Mo_{11}\}$ group is also shown which is formally a combination of 5 half $\{Mo_2\}$ linker groups and one $\{Mo(Mo_5)\}$ group.

It is remarkable that a molecular system as described above has icosahedral symmetry despite being comprised of more than 500 atoms. The giant cluster, with its 60 MoO_6 subunits or 12 related $\{(Mo)^0(Mo_5)^I\}$ pentagons, represents a topological model for spherical viruses, e.g. the most simple satellite tobacco necrosis virus (STNV), which has only 60 identical protein subunits coded by only one gene, contains only 12 pentagonal capsomers (morphology units, each consisting of five protomers; for details see [3, 15]).

In further studies the concept of connecting the pentagonal $\{(Mo)Mo_5\}$ with $\{Mo^V_2O_4\}^{2+}$ 'linkers' has been extended further by the substitution of these 'linkers' with 30 linking Fe^{III} centres by means of a simple, related synthesis, i.e. by reaction of the (larger) $\{Mo_{132}\}$-type cluster anion ($\{Mo_{102}Fe_{30}\}$) with an aqueous solution containing Fe^{III} centres, see Fig.3. In this way we have been able to elucidate more about the substitution and the construction principles behind the spherical cluster systems. In the spherical $\{Mo_{102}Fe_{30}\}$ cluster, as expected, the central Mo atoms of the 12 $\{(Mo)^0(Mo_5)^I\}$ pentagons span an icosahedron (Fig. 3.), while the 30 Fe atoms as well as the 30 centres of the Mo^V_2 groups form an icosidodecahedron. The special interest in this cluster system is also due to its magnetochemistry which is in principle governed by an only small antiferromagnetic exchange coupling between the 30 high-spin ($S = 5/2$) Fe centres. Incidentally, the (smaller) $\{(Mo)^0(Mo_5)^I(Fe_{5/2})^{II}\}_{12}$-type cluster represents the discrete cluster species with the largest number of paramagnetic centres synthesized to date (Fig. 5.3.)

Although the ring-shaped clusters have been considered using the empirical $\{Mo_{11}\}$ description, the structure of these systems can be expressed in terms of three other

building units of the form {Mo$_2$} {Mo$_8$} and {Mo$_1$} (formally the {Mo$_{11}$} group comprises one {Mo$_8$}, one {Mo$_1$} and two half {Mo$_2$} groups – Fig. 5.4.) In this way the discrete wheel-shaped clusters, such as [Mo$_{154}$O$_{462}$H$_{14}$(H$_2$O)$_{70}$]$^{14-}$, can be formulated as [{Mo$_2$}$_{14}${Mo$_8$}$_{14}${Mo$_1$}$_{14}$]$^{14-}$ [{Mo$^{VI}_2$O$_5$(H$_2$O)$_2$}$^{2+}_{14}${Mo$^{VI/V}_8$O$_{26}$($_3$-O)$_2$H(H$_2$O)$_3$Mo$^{VI/V}$}$^{3-}_{14}$]$^{14-}$. Each of the 14 basic {Mo$_8$} building blocks contains the central pentagonal-bipyramidal {MoO$_7$} polyhedron which is symmetrically connected to five MoO$_6$ octahedra by edge sharing resulting in the {(Mo)^0(Mo$_5$)^I} pentagon mentioned above. Four of these MoO$_6$ octahedra are linked to two further MoO$_6$ octahedra via corners to form the {Mo$_8$}-type block. Starting from the {Mo$_8$} group the complete {Mo$_{11}$}$_{14}$-type ring can be built up according to the following scheme: (1) The two MoO$_6$ octahedra which are not directly connected to the central MoO$_7$ bipyramid are fused to two neighbouring {Mo$_8$} groups via corners. (2) Neighbouring {Mo$_8$} groups are additionally fused together by the {Mo$_2$} groups (which are important for interesting reactivity studies on the cluster as these groups can be removed without changing the overall shape of the cluster[10]), thus completing the inner-ring parts of the upper or lower half of the ring structure which are both built up in the same way.   The complete ring system is constructed when the second half is rotated around 360/14° relative to the first and fused to it through {Mo$_1$} units which are located at the equator of the (complete) ring (Fig. 5.4). Furthermore an even larger ring-shaped cluster than the tetradecameric {Mo$_{11}$}$_{14}$ {Mo$_{154}$} type with a hexadecameric structure ({Mo$_{11}$}$_{16}$ {Mo$_{176}$}) can also be obtained. It correspondingly contains 16 instead of 14 {Mo$_{11}$} blocks or sets of each of the three mentioned building groups of the type {Mo$_8$}, {Mo$_2$} and {Mo$_1$}, respectively but retains the same basic structure as for the smaller {Mo$_{154}$}-based ring but with a decreased curvature of the ring [14].
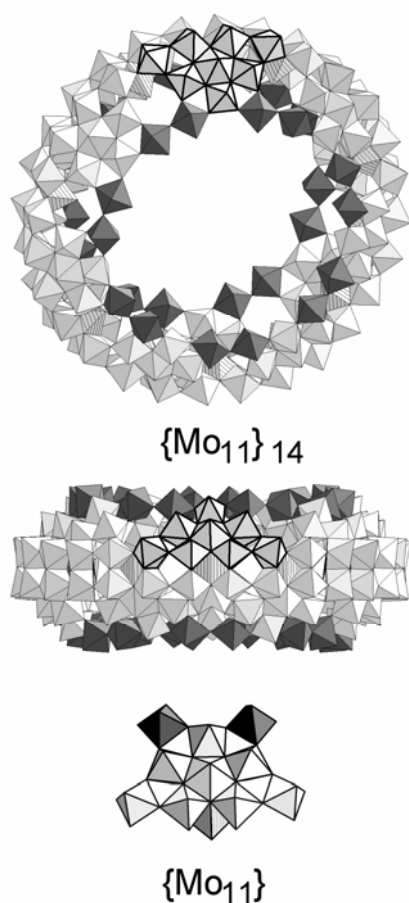

{Mo$_{11}$}$_{14}$

{Mo$_{11}$}

Figure 5.4. Top and side-on polyhedral-based representations of the {Mo$_{11}$}$_{14}$ {Mo$_{154}$} type cluster. The polyhedra forming the {Mo$_8$} groups are highlighted with thick lines and the {Mo$_2$} groups are shown as the black polyhedra, whereas the equatorial {Mo$_1$} groups are show as hatched polyhedra.   Below these representations an isolated {Mo$_{11}$} group is shown with the component polyhedra which form the {Mo$_8$}, {Mo$_2$} and {Mo$_1$} groups represented as above. [Note: 1 {Mo$_{11}$} = 1{Mo$_8$} + 2 x 0.5 {Mo$_2$} + 1{Mo$_1$}]

Precipitation and isolation of giant cluster anions, mainly those of the {Mo$_{11}$}$_n$ (n = 14, 16) type with extreme solubility (due to a large number of H$_2$O ligands, see Fig. 24), caused difficulties for chemists in the past, and also during the initial phase of our related investigations. Generations of chemists have tried, for instance, without success, to isolate pure crystalline compounds (or even obtain a few crystals) from the relevant molybdenum blue solutions, which mainly contain the above-mentioned highly soluble giant wheel-type cluster anions {Mo$_{11}$}$_n$ (n = 14, 16).

Nonetheless, the presence of electrolytes in a relatively high concentration has been found to be a good route to producing crystalline material. Our procedure allows the precipitation of the discrete $\{Mo_{11}\}_{14}$- and $\{Mo_{11}\}_{16}$-type clusters and related compounds with chain and layer structures in a high yield on a reasonable time scale in pure and crystalline form [17-20].

Through this work it has been shown that a huge variety of giant polyoxometalate clusters can be formed according to a type of unit construction under one-pot conditions, and furthermore, that both the giant-wheel shaped and spherical (Fe-based) clusters can be linked to form solid state structures (the linking of such structures is beyond the scope of this article but itself represents a very interesting area of this chemistry; for more information the reader is directed towards refs 10-12). On the basis of a variety of linkable building units, such as the pentagonal $\{(Mo)^0(Mo_5)^I\}$ type, and different types of linkers including paramagnetic centres, fascinating new possibilities present themselves e.g. for structural chemistry, supramolecular chemistry, materials science, and especially magnetochemistry. It is important to note that there are several control parameters, namely the degree of reduction and the pH of the solution, which influence the kind of $\{(Mo)^0(Mo_5)^I(Mo_5)^{II}\}$ blocks formed. In this way icosahedral structures (with C_5-type $\{Mo_{11}\}$ building blocks) or tetra-/hexadecameric ring structures (with C_s-type $\{Mo_{11}\}$ groups) can be deliberately obtained. These control parameters allow us to literally 'play with the pentagons' in the formation of the clusters which form spherical or ring shaped topologies.

However the question of exactly WHY these cluster systems were discovered at all still remains. This can be highlighted by considering the simplicity of the constituent building blocks and, therefore, the literally hundreds, maybe thousands, of condensed metal oxygen fragments with varying charges and symmetries that could exist in a solution of partly reduced molybdate at certain pH values. To answer this question we must consider a solution with many hundreds of different types of linkable units present in solution and smaller, building block species in equilibrium with large species (it should be noted that in poloxomolybdate chemistry this equilibrium is attained in a matter of minutes or hours). Perhaps the answer lies in with the fact that the pentagonal unit facilitates the formation of a curved geometrical system with no edges. Now, when one considers the formation of rigid pentagonal units in solution and the reaction through to the product – one can see that a closed cluster with no edges is uniformly reactive (this excludes the difference between the inner and outer side of the ring cluster which *do*, are certain circumstances react differently) and, therefore, harder to decompose (if it is rigid) than a cluster with many edges and no rigidity. In summary the combination of rigid units with pentagonal symmetry may result in many hundreds of species, but it is likely that only the structurally uniform, most stable species are likely crystallise. In this way the equilibrium can be pulled towards the precipitation of closed geometrical systems with no edges – i.e. clusters with ring or spherical topology, this hypothesis is summarized in Fig. 5.5.
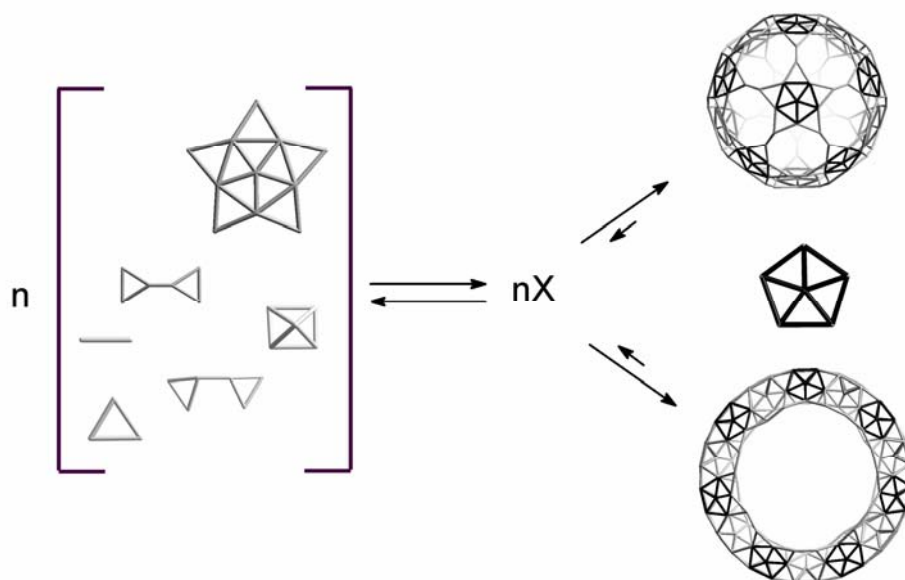
Figure 5.5. A schematic showing the potential for many types of polyoxometalate building blocks in solution with the pentagon-based units forming closed units (and therefore more difficult to decompose, all things being equal, than cluster a system that had well defined edges and corners). On the left-hand-side the vast number of hypothesised different building units present in solution, along with the pentagonal units are shown. Then our hypothesized equilibrium between these units and various clusters in solution is shown. Finally on the right hand side the clusters with pentagonal building blocks with closed geometries are depicted with an equilibrium which is in favour of the close-spherical / ring-shaped cluster system.

The future of this type of chemistry and approach does appear to have great potential in the synthesis of complex entities under one pot reaction conditions, but one observation seems clear- we still have a fantastic amount to learn from nature in our quest to synthesise man-made super-molecules.

Acknowledgements

References

[1]   P. R. Ashton, M. C. T. Fyfe, S. K. Hickingbottom, S. Menzer, J. F. Stoddart, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **1998**, *4*, 577-589

[2]   S. Warren (1997), Designing Organic Synthesis, Wiley, New York

[3]   L. Liljas, B. Strandberg (1984) In: Jurnak FA, McPherson A (eds) Biological Macromolecules and Assemblies, Vol. 1, Virus Structures. Wiley, New York, p 97

[4]   L. Stryer (1995), Biochemistry, 4 edn. W.H. Freeman & Co.

[5]   Coxeter HSM (1969) Introduction to Geometry. Wiley, New York

[6]   R. Penrose (1990), The Emperor's New Mind, Vintage, London, p173-174.

[7]   Krätschmer W, Schuster H (eds) (1996) Von Fuller bis zu Fullerenen, Beispiele einer interdisziplinären Forschung. Vieweg, Braunschweig

[8]   H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature*, **1985**, *318*, 162-163

[9]   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. Engl.*, **1995**, *34*, 2122-2124

[10]   L. Cronin, P. Kögerler, A. Müller, *J. Solid State Chem.* **2000**, *152*, 57-67.

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

[12]   A. Müller, P. Kögerler, H. Bögge, *Struct. Bond.* **2000**, *96*, 203-236.

[13]   A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann, F. Peters, *Angew. Chem. Int.   Ed.* **1998**, *37*, 3360-3363

[14]   A. Müller, S. Sarkar, H. Bögge, M. Schmidtmann, Sh. Sarkar, P. Kögerler, B. Hauptfleisch, S. Q. N. Shah, A. Trautwein, V. Schünemann (1999) *Angew. Chem. Int. Ed.* **1999**, *38,* 3238-3241

[15]   D. Voet, J. G. Voet (1995) Biochemistry, 2nd edn. Wiley, New York b) B. Alberts, D. Bray, J. Lewis, M. Raff, K. Roberts, J. D. Watson (1994) Molecular Biology of the Cell, 3rd edn. Garland, New York

[16]   A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann, C. Beugholt, P. Kögerler, C. Lu , *Angew. Chem. Int. Ed.* **1998**, *37*, 1220-1223

[17]   A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann, C. Beugholt, S. K. Das, F. Peters, *Chem. Eur. J.* **1999**, *5,* 1493-1502

[18]   A. Müller, M. Koop, H. Bögge, M. Schmidtmann, C. Beugholt, *Chem. Commun.,* **1998** 1501-1502

[19]   A. Müller, S. K. Das, H. Bögge, C. Beugholt, M. Schmidtmann, *Chem. Commun.,* **1999**, 1035-1036

[20]   A. Müller, S. K. Das, V. P. Fedin, E. Krickemeyer, C. Beugholt, H. Bögge, M. Schmidtmann, B. Hauptfleisch, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1187-1192