

Towards the construction of mesoscopic species with emergent and functional properties via the derivatisation of molybdenum-oxide ‘Giant-Wheel’ clusters

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Dedicated to Prof. Dr Dirk Walther on the occasion of his 60th birthday

Abstract

Polyoxometalate chemistry has proved to be an extraordinary source of a large variety of compounds, clusters and solid-state structures—these are built using very simple metal oxygen fragments linked together in an enormous variety of modes. Herein we focus on the ‘Giant-Wheel’ clusters which contain 154 and 176 Mo atoms and examine the variety of structural modifications that has been achieved to date with these systems. The generation of structural vacancies (here referred to as defects), substitution of ligands, and incorporation of hetero-metallic centres offers many fascinating possibilities with respect to the targeted functionalisation of these species for a pre-determined function and application. Furthermore, evidence is presented which suggests the identity of the most labile and, therefore, most easily derivatised units present in these systems. The consequences of this assignment are then discussed in the context of inter- (formation of layers and chains) and intra- (assembly inside the cavity) molecular growth. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The synthesis and manipulation of systems that exhibit a pre-designed functionality is one of the greatest challenges facing (natural) scientists today. Indeed, an examination of the literature reveals numerous papers ranging from solid-state physics [1] through to chemistry [2] and biology [3] that are aiming towards achieving this. In general, successive steps of synthesis, isolation and purification can achieve the construction of molecular architectures with functionality from the very small, to the very

large. Consequently, the method used by organic chemists often follows this route, starting from a retro-synthetic analysis of the target molecule. In principle, with this approach, any structure may be built but it is obvious that at a certain level of complexity, especially in the case of highly symmetrical giant species, the synthesis would become practically impossible [4].

In nature, complex molecular systems with functionality, e.g. proteins, are formed in a sequence of steps under dissipative conditions, i.e. far from thermodynamic equilibrium (based on a combination of step-wise and self-organised syntheses) [5]. The challenge for the chemist is to synthesise correspondingly complex species by means of multi-component one-pot reactions, and thus be exempt from the tedious

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separation and intermediate purification steps associated with construction, ‘from the bottom up’, atom-by-atom of the target molecule. In this respect, polyoxometalates represent a paradigm in which the breadth and diversity of the species formed, with structurally conserved units, is almost unprecedented [6]. As such, polyoxometalate chemistry exemplifies extraordinary model systems in which novel types of molecular growth processes lead to a huge variety of compounds, with unusual structures and properties. These processes can be described using a set of combinatorially linkable building units ‘present’ in solution as a basis. The units can be considered to be real or come from a ‘virtual library’, with the related intermediates becoming available under the synthetic conditions chosen. A pertinent example showing the effect of real units, which facilitate the formation of virtual units, is illustrated by some of our recent work in the construction of spherical clusters, or Keplerates [7,8]. These spherical clusters have the formula $[\text{Mo}_{72}^{\text{VI}}\text{Mo}_{60}^{\text{V}}\text{O}_{372}(\text{MeCO}_2)_{30}(\text{H}_2\text{O})_{72}]^{42-}$ ($\{\text{Mo}_{132}\}$) and consist of two types of building block; 12 pentagonal $\{(\text{Mo})(\text{Mo}_5)\}$ units and 30 $\{\text{Mo}_2^{\text{V}}\text{O}_4\}^{2+}$ units (this type of $\{\text{Mo}_2^{\text{V}}\text{O}_4\}^{2+}$ unit is formed only in the presence of stabilising acetate ligands). In this system the formation of the $\{\text{Mo}_2^{\text{V}}\text{O}_4\}^{2+}$ units is able to direct the formation of the $\{(\text{Mo})(\text{Mo}_5)\}$ pentagon which does not exist as an independent unit [7,8]. In this paper we will examine approaches to the derivatisation and functionalisation of the ‘Giant-Wheel’ $\{\text{Mo}_{154}\}$ and $\{\text{Mo}_{176}\}$ [9–11] type clusters with a view to exploring the possibility of constructing complex molecular systems with a pre-designed functionality.

2. Important factors for the construction and derivatisation of mesoscopic species

To examine the ultimate aim of this work, i.e. to be able to pre-design a molecular system of mesoscopic dimensions with functionality, it is informative to *consider the optimal conditions* for derivatisation and functionalisation of fragments leading to a huge variety of structures. These are given below:

- The potential of the system to generate a versatile library of linkable units.
- The ability to generate groups (intermediates) with high free enthalpy to drive polymerisation or growth processes, e.g. by formation of H_2O .
- The possibility for structural change in the building units or blocks.
- The ability to include hetero-metallic centres in the fragments.
- The possibility to form larger groups which can be linked in different ways.
- The ability to control the structure-forming processes using templates.
- The ability to generate structural defects in reaction intermediates (e.g. leading to lacunary structures) e.g. by removing building blocks from (large) intermediates due to the presence of appropriate reactants.
- The ability to localise and delocalise electrons in different ways in order to gain versatility.
- The ability to control and vary the charge of building parts (e.g. by protonation, electron transfer reactions, or substitution) and to limit growth by the abundance of appropriate terminal ligands.
- The possibility of generating fragments with energetically low-lying unoccupied molecular orbitals.

3. Synthetic approach to polyoxometalate clusters

Although a detailed explanation of the synthetic routes to the ‘Giant-Wheel’ clusters is beyond the scope of this article, the main parameters that must be considered in the synthesis of these systems are listed and briefly discussed. Therefore, each new derivative of the ‘Giant-Wheel’ cluster is considered along with the main synthetic ideas. By considering the synthesis in this way we can place it into its chemical context and, consequently, propose new synthetic strategies to a given structural type. Recently, a novel approach to the syntheses of $\{\text{Mo}_{154}\}$ type clusters has dramatically improved the yield and crystallisation time and the reader is directed towards this literature for the synthetic starting points [12,13].

Generally, the approaches used to produce high nuclearity molybdenum-oxide based clusters are extremely simple, consisting of acidifying an aqueous solution containing molybdate ions and its subsequent reduction. (This approach is extremely well known with solutions of molybdenum blue being instantaneously obtained by the reduction of Mo^{VI} type species in acid solutions ($\text{pH} \leq 3$)—in fact it has been shown by us previously that these solutions

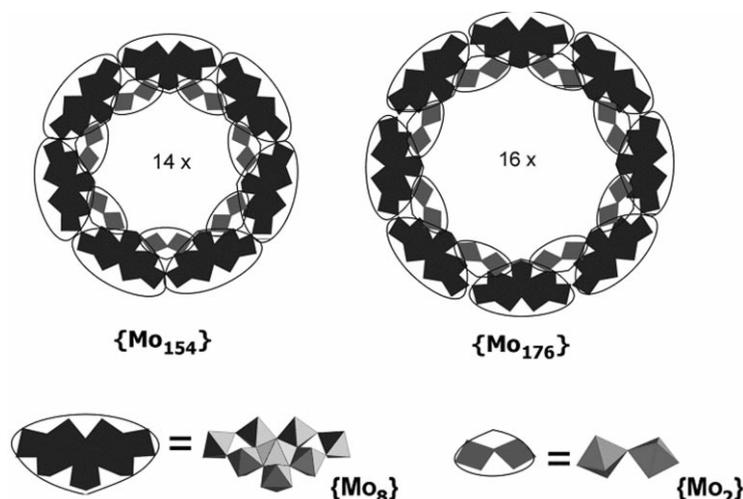


Fig. 1. A schematic of the upper halves of the tetradecameric $\{\text{Mo}_{154}\}$ and the hexadecameric $\{\text{Mo}_{176}\}$ 'Giant-Wheel' clusters. The $\{\text{Mo}_8\}$ and $\{\text{Mo}_2\}$ building blocks are shown below. The equatorial $\{\text{Mo}_1\}$ building blocks, which connect the two sides of the 'Giant-Wheels' together are not visible in this representation for clarity.

consist of polyoxometalate clusters with 'Giant-Wheel' building blocks [14].) Despite the simplicity of the system there are still a number of control parameters and these are summarised below:

- concentration of molybdate;
- type of reductant;
- type of electrolyte;
- electrolyte concentration;
- pH value;
- temperature.

In addition to these parameters a variety of heteroatoms and other species may be incorporated into the system, however the main three control parameters are the pH value, concentration of molybdate, and electrolyte concentration. Furthermore, the use of templates can play a key role in the construction of new types of systems [15].

4. Archetypal $\{\text{Mo}_{154}\}$ and $\{\text{Mo}_{176}\}$ type 'Giant-Wheel' clusters

Using reaction conditions of $\text{pH} \sim 1$, with a concentration of Na_2MoO_4 of ca. 0.5 M and a degree of reduction of between 1 and 20% a solution is generated which yields a 'Giant-Wheel' type cluster species, for example, comprising 154 Mo atoms

of formula $[\text{Mo}_{154}\text{O}_{462}\text{H}_{14}(\text{H}_2\text{O})_{70}]^{14-}$; see Fig. 1 (this can be compared to the formula of the original structure of the 'Giant-Wheel' cluster, $[\text{Mo}_{154}(\text{NO})_{14}\text{O}_{448}\text{H}_{28}(\text{H}_2\text{O})_{70}]^{28-}$; see Table 1).

Overall, the complete ring system consists of 140 MoO_6 octahedra and 14 pentagonal bipyramids of the type $\{\text{MoO}_7\}$; see Fig. 1. The wheel can be best described as a tetradecamer comprising 14 basic $\{\text{Mo}_8\}$ units with a central $\{\text{MoO}_7\}$ group. This $\{\text{MoO}_7\}$ unit is symmetrically connected to five $\{\text{MoO}_6\}$ octahedra by edge sharing resulting in a $\{\text{Mo}/\text{Mo}_5\}$ pentagon. (It should be noted that any toroidal system, such as the ring-cluster discussed here, requires a five-fold symmetry element to form the overall toroidal or spherical geometry—this is also true for clusters with a spherical topology [7,8].) Four of the $\{\text{MoO}_6\}$ octahedra are linked to further $\{\text{MoO}_6\}$ octahedra via corners to form the $\{\text{Mo}_8\}$ unit described above.

Continuing from the $\{\text{Mo}_8\}$ unit the complete $\{\text{Mo}_{154}\}$ cluster ring is built up as follows: (i) the two MoO_6 octahedra which are not directly connected to the central MoO_7 bipyramid are fused to neighbouring $\{\text{Mo}_8\}$ units through corners; (ii) neighbouring $\{\text{Mo}_8\}$ groups are additionally fused together by the $\{\text{Mo}_2\}$ units, thereby completing the inner-ring parts of the upper and lower half of the ring structure; (iii) the complete ring is constructed when the second half

Table 1
 ‘Giant-Wheel’ clusters and derivatives: building units and bond valence sum values deduced from the structures

Compound with approximate crystal water content	Building units ^a	Structure	BVS ^b (Mo)	BVS ^c (μ_3 -O)	Reference
Na ₂₆ [Mo ₁₄₂ O ₄₃₂ (H ₂ O) ₅₈ H ₁₄]-ca. 300 H ₂ O	{Mo ₂ } ₈ {Mo ₈ } ₁₄ {Mo ₁ } ₁₄	Discrete rings	5.6	(1.4)	[13]
(NH ₄) ₂₈ [Mo ₁₅₄ (NO) ₁₄ O ₄₄₈ H ₁₄ (H ₂ O) ₇₀]-ca. 350 H ₂ O ^d	{Mo ₂ } ₁₄ {Mo ₈ } ₁₄ {Mo ₁ } ₁₄	Discrete rings	5.7	1.2	[10]
Na ₁₄ [Mo ₁₅₄ O ₄₆₂ H ₁₄ (CH ₃ OH) ₈ (H ₂ O) ₆₂]-ca. 400 H ₂ O-ca. 10 CH ₃ OH ^e	{Mo ₂ } ₁₄ {Mo ₈ } ₁₄ {Mo ₁ } ₁₄	Discrete rings	5.5	1.2	[21]
Na ₁₅ {0.5[Mo ₁₅₄ O ₄₆₂ H ₁₄ (H ₂ O) ₇₀]-0.5 × [Mo ₁₅₂ O ₄₅₇ H ₁₄ (H ₂ O) ₆₈]}-ca. 400 H ₂ O	{Mo ₂ } ₁₄ {Mo ₈ } ₁₄ {Mo ₁ } ₁₄	Two different discrete rings, one of which possesses a defect	5.6 5.6	1.2 1.2	[12]
Li ₁₆ [Mo ₁₇₆ O ₅₂₈ H ₁₆ (H ₂ O) ₈₀]-ca. 400 H ₂ O ^d	+ {Mo ₂ } ₁₃ {Mo ₈ } ₁₄ {Mo ₁ } ₁₄ {Mo ₂ } ₁₆ {Mo ₈ } ₁₆ {Mo ₁ } ₁₆	Discrete rings	5.6	1.3	[10,11]
Na ₁₆ [Mo ₁₇₆ O ₅₂₈ H ₁₆ (CH ₃ OH) ₁₇ (H ₂ O) ₆₃]-ca. 600 H ₂ O-ca. 30 CH ₃ OH	{Mo ₂ } ₁₆ {Mo ₈ } ₁₆ {Mo ₁ } ₁₆	Discrete rings	5.7	1.3	[20]
Na ₂₄ {0.5[Mo ₁₄₄ O ₄₃₇ H ₁₄ (H ₂ O) ₅₆]-0.5 × [Mo ₁₄₄ O ₄₃₇ H ₁₄ (H ₂ O) ₆₀]}-ca. 350 H ₂ O	{Mo ₂ } ₉ {Mo ₈ } ₁₄ {Mo ₁ } ₁₄ + {Mo ₂ } ₉ {Mo ₈ } ₁₄ {Mo ₁ } ₁₄	Discrete rings with defects and chains built up by rings with defects	- ^f	- ^f	[16]
Na ₂₄ [Mo ₁₄₄ O ₄₃₇ H ₁₄ (H ₂ O) ₅₆]-ca. 250 H ₂ O ^d	{Mo ₂ } ₉ {Mo ₈ } ₁₄ {Mo ₁ } ₁₄	Chains built up by rings with defects	5.8	1.2	[23]
Na ₂₂ [Mo ₁₄₆ O ₄₄₂ H ₁₄ (H ₂ O) ₅₈]-ca. 250 H ₂ O	{Mo ₂ } ₁₀ {Mo ₈ } ₁₄ {Mo ₁ } ₁₄	Chains built up by rings with defects	5.6	1.2	[12]
Na ₁₆ [Mo ₁₅₂ O ₄₅₇ H ₁₄ (H ₂ O) _{66.5}]-ca. 300 H ₂ O	{Mo ₂ } ₁₃ {Mo ₈ } ₁₄ {Mo ₁ } ₁₄	Layers built up by rings with defects	5.6	1.2	[16]
Na ₂₁ [Mo ₁₅₄ O ₄₆₂ H ₁₄ (H ₂ O) ₅₄ (H ₂ PO ₂) ₇]-ca. 300 H ₂ O	{Mo ₂ } ₁₄ {Mo ₈ } ₁₄ {Mo ₁ } ₁₄	Layers with attached H ₂ PO ₂ ⁻ groups	5.6	1.2	[24]
Na ₆ [Mo ₁₂₀ O ₃₆₀ (H ₂ O) ₆₀ H ₁₂ {Pr(H ₂ O) ₅ }]·200 H ₂ O	{Mo ₂ } ₆ {Mo ₈ } ₁₂ {Mo ₁ } ₁₂	Distorted ring with 6 Pr ³⁺ ions attached	5.6	1.2	[28]

^a The general formula for the discrete pure molybdenum-oxide based unit is $[\{Mo_2^VI O_5(H_2O)_2\}_{b-x}^{\{Mo_8^{VI} O_{26}(\mu_3-O)_2 H_m(H_2O)_3 Mo^{VI} O_4\}^{(4-m)-}}\}_b]^{(2b-bm+2x)-} \equiv [\{Mo_2\}_{b-x}\{Mo_8\}_b\{Mo_1\}_b]^{(2b-bm+2x)-}$ (b = number of building units per set = number of compartments referring to ref. [16] Fig. 3 = number of protonations at the equatorial μ_3 -O atoms or in the $\{(\mu_3-O)_2 O_2\}$ compartment (for $m = 1$) = half of the (formal) number of Mo^V centres; x = number of defects or missing $\{Mo_2\}^{2+}$ units).

^b Average BVS value for the Mo centers which span the b incomplete $\{Mo_5O_6\}$ -type double cubanes, built up by (parts of) the $\{Mo_8\}$ and $\{Mo_1\}$ units ref. [16] Fig. 3. The (formal) number of Mo^V centres per ring for all compounds is $2b$ (or two per compartment) according to the related constant BVS (Mo) values and other experimental data (see text).

^c Average BVS value for the μ_3 -O atoms of the $b = 14$ or 16 $\{(\mu_3-O)_2 O_2\}$ -type compartments ref. [16] Fig. 3, which indicates protonation at the equatorial μ_3 -O atoms or within the $\{(\mu_3-O)_2 O_2\}$ compartments. The finally accepted value for the number of protons m per compartment is 1 mainly according to the results of the numerous cation analyses. This value corresponds to a disorder of the kind that only one of the two μ_3 -O atoms of a compartment is protonated. This situation ($m = 1$) is also more plausible as the other possibility ($m = 2$) leads to a rather small H–H distance in the compartment (compare W.H. Baur, On H···H distances and the van der Waals radius of hydrogen in inorganic and organic compounds, Acta. Cryst. B48 (1992) 745–746).

^d Formulas of some earlier reported compounds corrected according to the now accepted type of protonation for compounds with $b = 14$ building units (tetradecameric case) or $b = 16$ (hexadecameric case).

^e Because of the rather high resolution of the crystal structure, Na⁺ positions could be determined for the first time, proving their importance for the structure formation.

^f The structure is not sufficiently resolved to calculate reasonable BVS values.

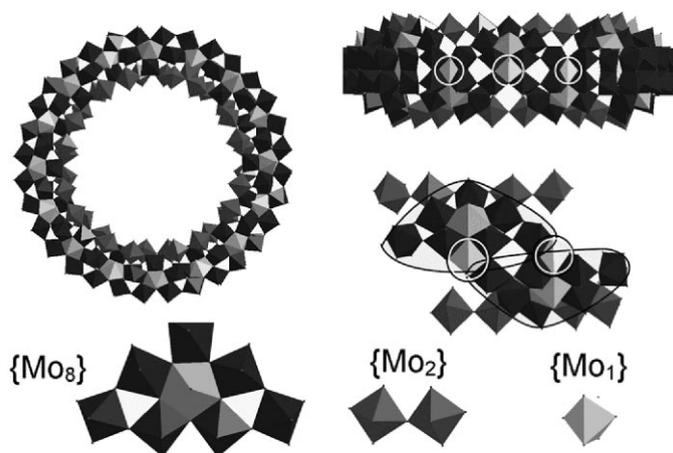


Fig. 2. A schematic showing the general architecture principle for the ‘Giant-Wheel’ type clusters, using the $\{\text{Mo}_{176}\}$ cluster (top view left-hand side and side view right-hand side) as an example. The structural building blocks for all the ‘Giant-Wheel’ clusters can be formulated as comprising $\{\text{Mo}_8\}$ units that are connected together via the $\{\text{Mo}_2\}$ units on the inner side of the wheel. Finally, the $\{\text{Mo}_1\}$ units form the equatorial plane of the ring linking the $\{\text{Mo}_8\}$ units together above and below the equator. These units are shown separately. A section of the cluster is shown which comprises $\{\text{Mo}_8\}_2\{\text{Mo}_2\}_4\{\text{Mo}_1\}_2$ units to highlight how the units are connected to each other—the $\{\text{Mo}_8\}$ units are outlined along with the $\{\text{Mo}_1\}$ units, which are circled.

is rotated around $360/14^\circ$ relative to the first and fused to it through the 14 $\{\text{Mo}_1\}$ groups, which are located at the equator of the complete ring; see Fig. 2. Using the general architecture principle for the ‘Giant-Wheel’ type clusters the structural building blocks, e.g. for the $\{\text{Mo}_{154}\}$ type cluster, can be deduced from the formula, $[\text{Mo}_{154}\text{O}_{462}\text{H}_{14}(\text{H}_2\text{O})_{70}]^{14-}$, in terms of the three different building blocks as $[\{\text{Mo}_2\}_{14}\{\text{Mo}_8\}_{14}\{\text{Mo}_1\}_{14}]^{14-}$.

The synthesis of the $\{\text{Mo}_{176}\}$ type cluster can be related to that of the tetradecameric $\{\text{Mo}_{154}\}$ cluster. The most important change is that this requires reaction conditions with a pH lower than 1 and the presence of an increased concentration of molybdate. The $\{\text{Mo}_{176}\}$ cluster can be broadly described as a hexadecamer with two extra $\{\text{Mo}_8\}$, $\{\text{Mo}_2\}$ and $\{\text{Mo}_1\}$ units, respectively, with a formula of $[\text{Mo}_{176}\text{O}_{528}\text{H}_{16}(\text{H}_2\text{O})_{80}]^{16-}$ which again, can be broken into the three types of building units, $[\{\text{Mo}_2\}_{16}\{\text{Mo}_8\}_{16}\{\text{Mo}_1\}_{16}]^{16-}$; see Figs. 1 and 2.

The deduction of the molecular formula (and the overall charge) for the first ‘Giant-Wheel’ presented a tremendous problem in the past. However, this information can now be routinely deduced from a combination of redox titrations, UV–Vis spectroscopy (the solution spectrum of the $\{\text{Mo}_{154}\}$ cluster gives an absorption at ca. 750 nm with $\epsilon \approx 6 \times 10^3 \text{ l mol}^{-1}$

$\text{cm}^{-1}/\text{Mo}^{\text{V}}$ centre, corresponding to an inter-valence charge transfer) and analysing structural data by calculating the bond-valence-sums for the molybdenum centres [16]. Using this information it has been found that the number of $\{\text{Mo}_8\}$ or $\{\text{Mo}_1\}$ units is equal to half the formal number of Mo^{V} centres and equal to the overall charge on the $\{\text{Mo}_{154}\}$ and $\{\text{Mo}_{176}\}$ clusters, respectively (except in the case of the first ‘Giant-Wheel’ structure which also incorporated NO as a ligand). There are formally 28 and 32 Mo^{V} centres corresponding to charges of 14 and 16 for the $\{\text{Mo}_{154}\}$ cluster ($\equiv [\{\text{Mo}_2\}_{14}\{\text{Mo}_8\}_{14}\{\text{Mo}_1\}_{14}]^{14-}$) and $\{\text{Mo}_{176}\}$ cluster ($\equiv [\{\text{Mo}_2\}_{16}\{\text{Mo}_8\}_{16}\{\text{Mo}_1\}_{16}]^{16-}$), respectively.

At the time of discovery and publication, the $\{\text{Mo}_{154}\}$ ‘Giant-Wheel’ type cluster represented the largest cluster to be structurally characterised by single crystal X-ray diffraction and gained a large amount of public interest and a metaphorical statement in the magazine *NewScientist* [17],

Big wheel rolls back the molecular frontier

This statement encompassed the enormous interest generated by the ‘Giant-Wheel’ cluster. This is because the cluster is of ‘mesoscopic’ dimensions, and as such, demonstrates potential to bridge the gap between the molecular world, characterised by

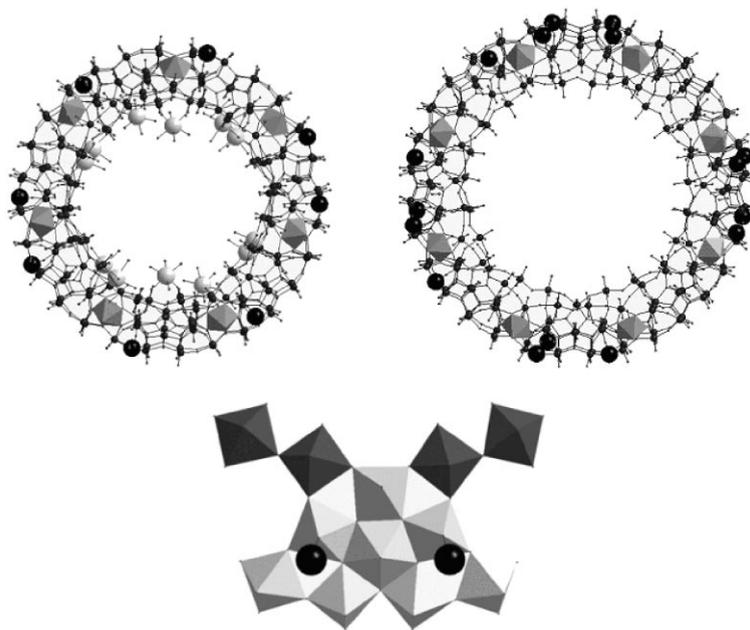


Fig. 3. Ball and stick representations of $\{\text{Mo}_{154}\}\cdot 8\text{MeOH}$ (left side) and $\{\text{Mo}_{176}\}\cdot 17\text{MeOH}$ type clusters (right side) with surface exchanged methanol molecules highlighted and the central pentagonal unit of each $\{\text{Mo}_8\}$ unit shown as polyhedron. The lower section shows the typical location of the methanol molecules on the $\{\text{Mo}_8\}$ unit. The positions of the located sodium ions in the crystal structure of the first compound are shown as grey spheres ($\{\text{Mo}_{154}\}\cdot 8\text{MeOH}$).

small molecules or ions, and a world of macroscopic compounds. (The term mesoscopic is used to define the intermediate size between the microscopic size of small molecules and macroscopic size of ‘bulk’ compounds, e.g. metal-oxides.) The unique features associated with the ‘Giant-Wheel’ clusters can be summarised as follows.

The $\{\text{Mo}_{154}\}$ and $\{\text{Mo}_{176}\}$ type clusters ($n = 14, 16$) exhibit interesting properties with many potential applications:

- They exhibit a nanometre-sized cavity, presenting new perspectives for a novel host–guest chemistry according to the different sites on the cluster surfaces.
- They have an extended hydrophilic inner and outer surface due to the presence of $5n$ H_2O ligands ($2n$ H_2O ligands belong to the $\{\text{Mo}_2\}$ and $3n$ H_2O ligands to the $\{\text{Mo}_8\}$ groups).
- They have a huge surface area; this explains in part their high affinity towards adsorbents such as charcoal or silk.
- They render a molecular model for catalytically active metal-oxides of industrial importance.
- The aqueous solution shows further aggregation tendencies: formation of colloids of ca. 40 nm hydrodynamic radius could be detected by means of dynamic light scattering and scanning electron microscopy for the precipitated species [18].
- The periphery of the cluster rings shows a high electron density with implications for the activation of small molecules co-ordinated to the surface sites.
- There are n electronically practically uncoupled $\{\text{Mo}_5\text{O}_6\}$ compartments of incomplete double-cubane type, each of which carries two delocalised 4d electrons, a situation which is comparable to a so-called electronic necklace corresponding to an electron-storage system where the uncoupled storage elements are threaded like pearls on a string. These compartment-delocalised electrons are responsible for the intense blue colour [16,19].
- It is possible to generate deliberately discrete and well-defined structural defects on the inner surface of the cluster ring by abstracting positively charged $\{\text{Mo}_2\}$ groups using special ligands, which have a high affinity to these groups (see below). This drastically changes both the reactivity and the shape.

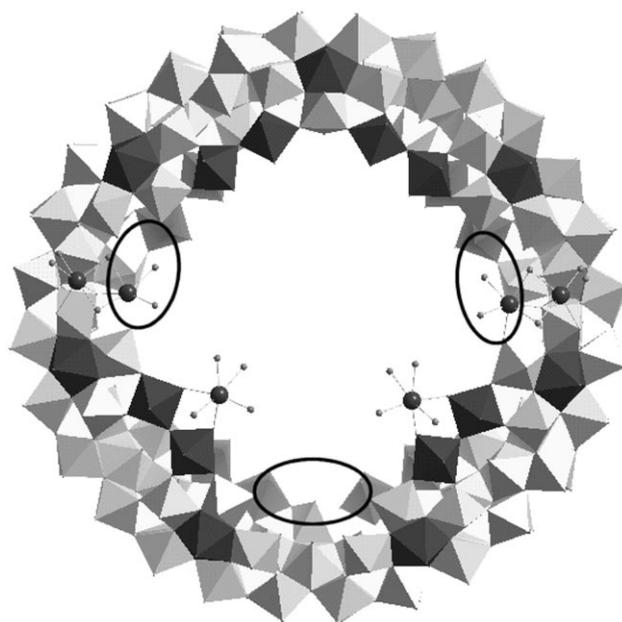


Fig. 4. Polyhedral representation of the high defect $\{\text{Mo}_{142}\}$ cluster. This ‘Giant-Wheel’ cluster has 6 defects per ring, 3 on the top side and 3 on the bottom. The absence of polyhedra represents a defect (only the defects on the top side are highlighted by an ellipse). There are six locations on each side of the ring that are occupied by sodium ions but only the locations of the sodium ions (octahedrally coordinated) on the top side of the ring are shown for clarity.

- The ring-shaped units can be linked according to a type of crystal engineering: assembly due to synergistically induced functional complementarity of distinct surface sites (see below).
- It is possible to place molecules or replace ligands, e.g. H_2O by CH_3OH [20–22], at different sites of the surface, in particular to replace up to two H_2O ligands at the $\{\text{Mo}_8\}$ groups (thereby changing the properties of the clusters) and to study direct reactions between the molecules placed inside the cavity.

Since the discovery of the original ‘Giant-Wheel’ cluster 12 related clusters have been synthesised and characterised by X-ray crystallography. The formula, building units, and bond valence sums are presented in Table 1.

5. Surface ligand exchange

Both types of the ‘Giant-Wheel’ clusters have a very large number of H_2O ligands present on the surface of the cluster; the $\{\text{Mo}_{154}\}$ cluster supports 70 H_2O ligands and the $\{\text{Mo}_{176}\}$ cluster 80 H_2O

ligands. As a result, it appears possible to exchange these ligands by those with similar donor properties, for example, CH_3OH . In the presence of CH_3OH it has been found that the $\{\text{Mo}_{154}\}$ and the $\{\text{Mo}_{176}\}$ rings can uptake 8 and 17 CH_3OH molecules, respectively, displacing H_2O ligands, as observed by single crystal X-ray crystallography (see Fig. 3) [20–22]. It is interesting to note that in both structures the CH_3OH ligands are *only observed* to replace the H_2O ligands that exist on one type of site (although the CH_3OH molecules were found to occupy only one type of site by X-ray crystallographic studies, this does not rule out the possibility of disorder over other sites—both in solution and in the solid-state [20–22]). This site occurs on the $\{\text{Mo}_8\}$ unit between the Mo polyhedra that is adjacent to the hole formed below the $\{\text{Mo}_2\}$ units. Furthermore, in the case of the $\{\text{Mo}_{154}\}\cdot 8\text{MeOH}$ type cluster several sodium ions were also located in the crystal structure—these were co-ordinated (at an occupancy of 50%) to the $\{\text{Mo}_2\}$ units. These results have indicated that by modelling (pattern matching, donor matching) the sites amenable to surface exchange it should be possible

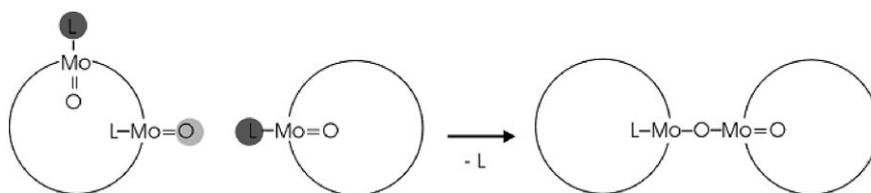


Fig. 5. Schematic representation of the basic assembly principle of the 'Giant-Wheel' shaped cluster units forming the networks and layers. The formation is based on the synergetically induced functional complementarity of the $\{\text{Mo}_2\}$ units $\text{O}=\text{Mo}(\text{L})$ (e.g. $\text{L} = \text{H}_2\text{O}, \text{H}_2\text{PO}_4^{2-}$) sites of their surfaces.

to utilise ligands with more than one donor atom. By functionalising the ring with multi-donor ligands it should be possible to attach ligands much more easily by taking advantage of the chelate effect. Such derivatives can then be extended to incorporate amphiphilic ligands with the head part exchanging the H_2O ligands that can in turn allow the complexation of other species onto and into the wheel by the tail of the ligand.

6. Introduction of defects and linking the 'Giant-Wheel' clusters to chain and layer networks

One extremely interesting observation is that under certain synthetic conditions it is possible to obtain 'Giant-Wheel' species based on the $\{\text{Mo}_{154}\}$ type

cluster which are structurally incomplete. These defects manifest themselves as missing $\{\text{Mo}_2\}$ units, but statistically these defects can sometimes be seen as under occupied $\{\text{Mo}_2\}$ units when the distribution suffers from rotational or translational disorder within the crystal structure. The most extreme case found to date has 6 defects [12,13] introduced into the 'Giant-Wheel' cluster, three on each side of the cluster; Fig. 4. In this case the synthetic conditions needed to isolate the $\{\text{Mo}_{142}\}$ species required a very large concentration of electrolyte (in this case ca. 2 M sodium ions present) at the time of crystallisation giving a compound with the formula $\text{Na}_{26}[\text{Mo}_{142}\text{O}_{432}(\text{H}_2\text{O})_{58}\text{H}_{14}]$, ($\equiv [\{ \text{Mo}_2 \}_8 \{ \text{Mo}_8 \}_{14} \{ \text{Mo}_1 \}_{14}]^{26-}$). This time the number of each type of building block is not identical as six $\{\text{Mo}_2\}^{2+}$ groups

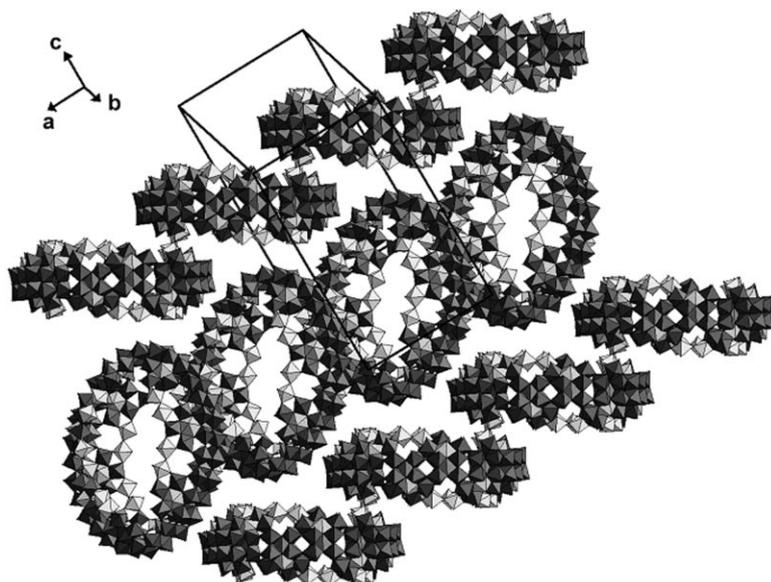


Fig. 6. A polyhedral representation of $\{\text{Mo}_{144}\}$ units linked to chains [23]. The linking occurs via the $\{\text{Mo}_2\}$ units (see Table 1).

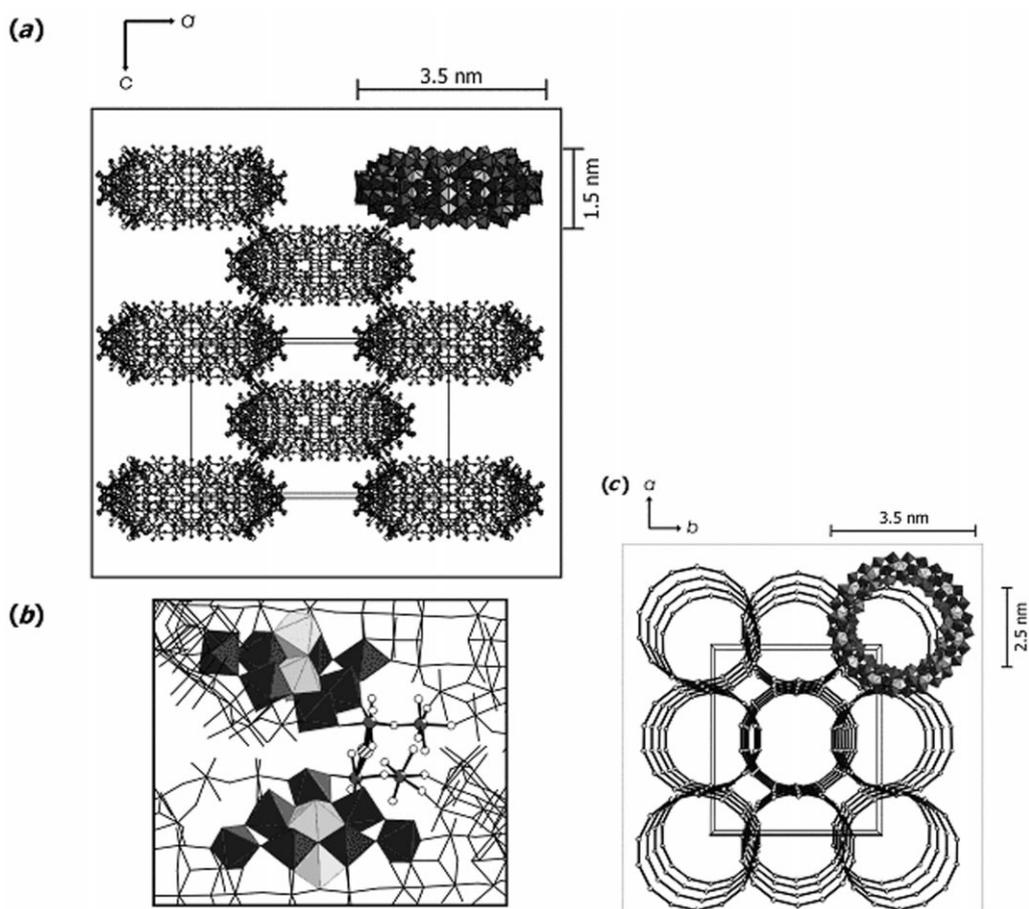


Fig. 7. (a) Ball and stick representation of the ‘packing’ of the linked rings in crystals of $Na_{16}[Mo_{152}^{VI}Mo_{28}^{V}O_{429}(\mu_3-O)_{28}H_{14}(H_2O)_{66.5}] \cdot XH_2O$ ($X \approx 300$) ($\{Mo_{152}\}$) viewed along the crystallographic *b* axis. Each ring is connected to surrounding rings via Mo–O–Mo bridges of the O=Mo–O–Mo–OH₂ units, thus forming layer networks parallel to the *ac* plane. One ring is shown as basic unit in polyhedral representation. (b) Detailed view of the bridging region between two cluster rings. One $\{Mo_8\}$ unit of each ring along with one $\{Mo_1\}$ unit is shown in polyhedral representation and one $\{Mo_2\}^{2+}$ ($=\{Mo_2^VI O_5(H_2O)_2\}^{2+}$) unit per ring in ball and stick representation. (c) Perspective view along the crystallographic *c* axis showing the framework with nanotubes that are filled with H₂O molecules and sodium cations. For clarity, only one ring is shown in a polyhedral representation. To represent the other rings only the equatorial $\{Mo_1\}$ units are given and connected [16].

have been removed increasing the negative charge of the ‘Giant-Wheel’ by 12. The increased charge, as a consequence of the defects, has increased the number of sodium ions associated with each ‘Giant-Wheel’ and it is not surprising that 12 positions were found in the crystal structure that were refined as under occupied sodium ions (a total of 6.4 sodium ions were found over 12 positions) [13]. It is interesting that the sodium ions were found to be ligated to the oxygen atoms of the remaining $\{Mo_2\}$ units or ligated to the oxygen atoms left in the defect sites.

It should be noted however, that as the introduction of defects increases the overall negative charge of the ‘Giant-Wheel’ cluster [12,13,16,23], the rings can be linked together into chains and layers *under related conditions* (see Table 1). In general, this type of linking reaction occurs by the condensation of the terminal $\{Mo_2\}$ -based H₂O–Mo=O groups on the rings with the H₂O ligands on the $\{Mo_2\}$ units, O=Mo–L (L = H₂O) (see Fig. 5). For example $\{Mo_{144}\}$ clusters [23] can be linked to chains (see Fig. 6) and $\{Mo_{152}\}$ clusters can be linked to form two-dimensional (2D)

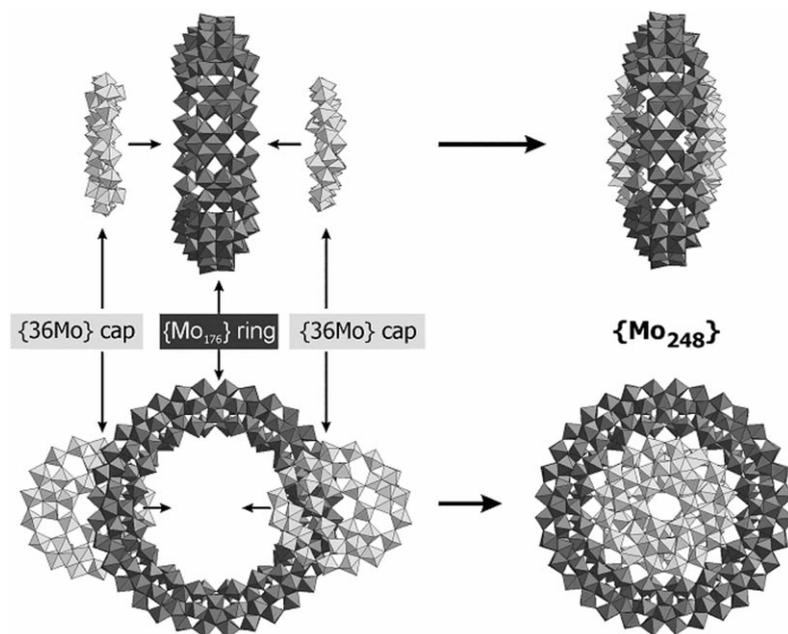


Fig. 8. A schematic representation of the growth process $\{Mo_{176}\} \rightarrow \{Mo_{248}\}$. The structure of one $\{Mo_{248}\}$ cluster can formally be decomposed into one $\{Mo_{176}\}$ ring and two $\{Mo_{36}O_{96}(H_2O)_{24}\}$ ‘hub-caps’.

layers in the construction of a layered compound (see Fig. 7). The assembly of the chain shown in Fig. 6 is thought to occur due to the increased negative charge resulting from the defects present in the ring which results from the loss of $\{Mo_2\}$ units. The existence of under-occupancy at the $\{Mo_2\}$ sites is now well established [12,13,23] and has been found to be promoted by the addition of ligands such as the formate anion which has been shown to extract the $\{Mo_2\}$ units from the inner surface of the $\{Mo_{154}\}$ type cluster. This abstraction has the secondary effect of causing a higher nucleophilicity at the $O=Mo(H_2O)$ sites of the $\{Mo_2\}$ units in the surrounding area [12,13,16]. In the case of the layered compounds [23,24] the assembly to layers has, so far, been achieved with two approaches:

- By producing defects [12,13,16] which increase the nucleophilicity (by increasing the local negative charge on the terminal oxygen ligand ($Mo=O$)) of the $\{Mo_2\}$ units that are still present on the cluster.
- By introducing an electron withdrawing bidentate ligand, e.g. $H_2PO_2^-$ (see Fig. 5) to the $\{Mo_2\}$ units

to increase the nucleophilicity on the $\{Mo_2\}$ -based $Mo=O$ group. In this case the $H_2PO_2^-$ acts as both the reducing agent (in the formation of the ‘Giant-Wheel’) as well as the bidentate ligand.

In the last process it can be considered that the reaction is facilitated by synergetically induced functional complementarity. Examination of the overall structure forms reveals the presence of 2D layers in which the cavities of the ‘Giant-Wheel’ cluster stack up on each other to form nanotubes which are filled with H_2O molecules and sodium cations (see Fig. 6).

7. Nucleation processes within a cluster cavity— from a $\{Mo_{176}\}$ to a $\{Mo_{248}\}$ cluster

To date, despite the increasing knowledge behind the reduction and synthesis of crystalline compounds containing ‘Giant-Wheel’ clusters, it is interesting that all the diverse formulations of the $\{Mo_{154}\}$ type analogues have not been repeated with the larger $\{Mo_{176}\}$ ring structure. One possible explanation for this observation is that the $\{Mo_2\}$ groups are more strained in the $\{Mo_{154}\}$ than in the $\{Mo_{176}\}$ wheel

due to the inclusion of more building groups. This is because the overall curvature is less in the $\{\text{Mo}_{176}\}$ than in the $\{\text{Mo}_{154}\}$ cluster. Therefore, any reactions that remove the $\{\text{Mo}_2\}$ groups from the $\{\text{Mo}_{176}\}$ cluster may be energetically unfavourable under the conditions which have been studied. This idea would also explain why no example of a defect or chain $\{\text{Mo}_{176}\}$ cluster has been observed.

It is extraordinary, therefore, that under special types of reducing conditions (using ascorbic acid as a reducing agent) [25,26] the $\{\text{Mo}_{176}\}$ cluster can be observed to grow—during this process two further $\{\text{Mo}_{36}\}$ units are added to each side of the cluster forming a spherical disk shaped cluster comprising 248 Mo atoms; see Fig. 8. This appears to be a remarkable result when it is considered that the larger wheel cluster ‘cap’ $[\text{Mo}_{36}\text{O}_{96}(\text{H}_2\text{O})_{24}]$ -type fragment is nearly identical to a segment of the solid-state structure of the compound $\{\text{Mo}_5\text{O}_{14}\}$; see Fig. 9 [27]. This extraordinary structure (the largest discrete inorganic structure to be characterised by single crystal X-ray diffraction to date) offers the possibility to model crystal growth under boundary conditions, especially the related nucleation process. Of particular importance is that the growth event can be considered to start from the inner $\{\text{Mo}_2\}$ groups; see Fig. 8.

8. Replacing the $\{\text{Mo}_2\}$ groups with electrophiles

Formally, the removal of a $\{\text{Mo}_2\}$ unit, by introducing defects, from the ‘Giant-Wheel’ type clusters should result in the negative charge increasing by two. Therefore, the introduction of defects into the ‘Giant-Wheel’ cluster systems provides a route to the specific derivatisation of the inner side of the cluster (this is because the defects only occur at the $\{\text{Mo}_2\}$ -type sites on the inside of the cluster) and should allow the incorporation of electrophilic substrates.

In a recent derivatisation of the $\{\text{Mo}_{154}\}$ cluster it has been shown that six of the $\{\text{Mo}_2\}$ groups can be completely replaced by $\{\text{Pr}(\text{H}_2\text{O})_5\}^{3+}$ moieties [28], resulting in a $\{\text{Mo}_{120}\text{Pr}_6\}$ -type ‘Giant-Wheel’ cluster; see Table 1 and Fig. 10. The $\{\text{Mo}_{120}\text{Pr}_6\}$ -type cluster consists also of characteristic sets of the three characteristic building blocks $\{\text{Mo}_2\}$, $\{\text{Mo}_8\}$ and $\{\text{Mo}_1\}$, but corresponding to the formula of the dodecameric cluster. Therefore, the incorporation of Pr^{3+} into the

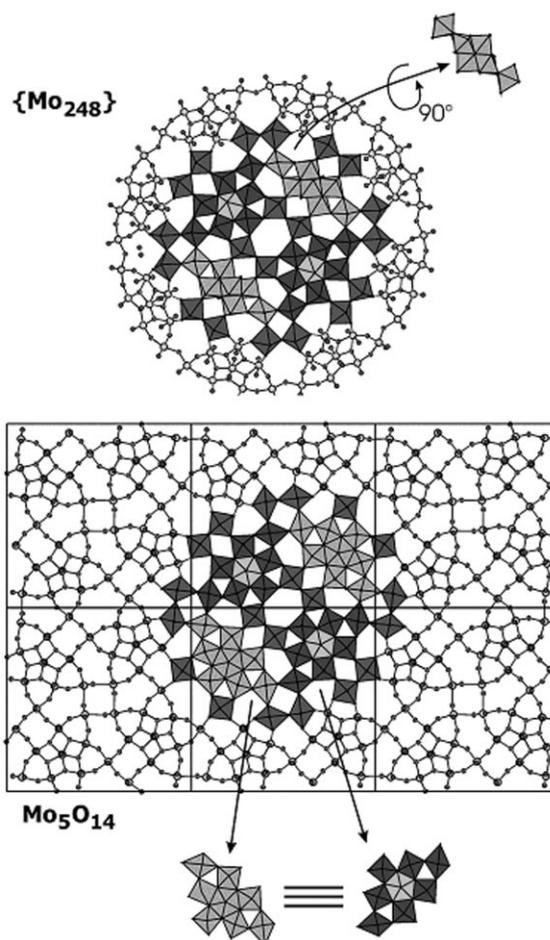


Fig. 9. A structural comparison of the hub-cap motif of the $\{\text{Mo}_{248}\}$ cluster (above) and the related segment of the solid state structure, $\{\text{Mo}_5\text{O}_{14}\}$ (below).

ring system has resulted in a ring with increased curvature. The main consequence of the increased curvature is shown as a decreased average diameter and ring size, as the number of building blocks that can be incorporated is smaller than compared to the $\{\text{Mo}_{154}\}$ ‘Giant-Wheel’ cluster; see Table 1.

9. Future aims

‘Giant-Wheel’ clusters exhibit an extraordinarily rich chemistry with respect to the types of derivatives that can be formed. Furthermore, in all the examples found to date, the most labile site for both electrophilic

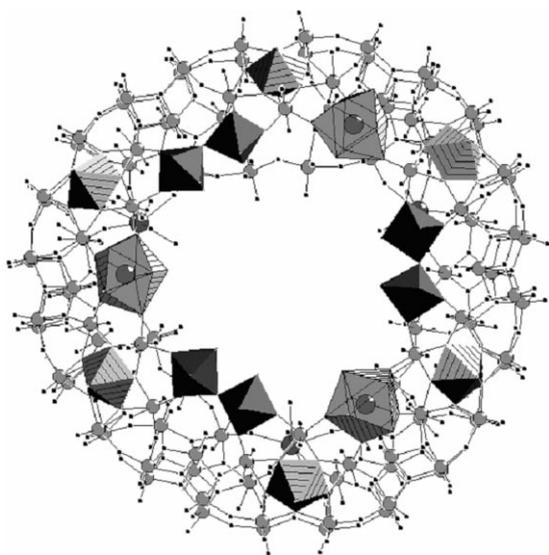


Fig. 10. A schematic showing the structure of $\{Mo_{120}Pr_6\}$ ‘Giant-Wheel’ cluster in ball and stick presentation (view along the crystallographic a axis). The PrO_9 polyhedra (the Pr atoms are shown in the centre of the polyhedra with hatched sides and open faces), the pentagonal bipyramids (shown as hatched polyhedra) and the $\{Mo_2\}$ units (shown as filled polyhedra) on the upper half of the wheel are shown in polyhedral representation.

and nucleophilic modification has been found to be the $\{Mo_2\}$ -type building unit which exists on the inside of the ‘Giant-Wheel’ type clusters.

Future work in this area will focus on the $\{Mo_2\}$ groups with the view to understanding how the derivatisation of these units can enable the incorporation of functionalities to allow:

- New types of host–guest systems for sequestration and anion sensors replacing/adding ligands to the $\{Mo_2\}$ units.
- New types of magnetic model systems via the replacement of the $\{Mo_2\}$ -type units with high-spin metal centres.
- The designed modification/defect generation of the $\{Mo_2\}$ -type units to synthesise *neutral* mesoporous solids.

A further challenge lies in the generation of systems with (complex) macroscopic structures by linking the ‘Giant-Wheel’ clusters in an *open* system [29]. Such approaches could help us to understand processes utilised by nature with respect to the self-organisation

of bio-molecules and biomineralisation, for example the growth of unicellular diatoms [30].

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