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Chemical design of homo- and heteronuclear polyoxomolybdate clusters †

S S Talismanov, I L Eremenko

Contents

I.	Introduction	555
II.	Key principles of the formation of polyoxometallate clusters	555
III.	Formation of cluster anions containing $\{Mo_{17}\}$ fragments	556
IV.	Interconversions of some polyoxomolybdates in organic solvents	558
V.	Molybdenum blues	561
VI.	Spherical systems (keplerates)	562
VII.	Spherical giant clusters as building blocks in chemical design	565
VIII.	Polyoxomolybdate clusters as nanoreceptors	567

Abstract. Data on the chemistry of the key types of large homo- and heteronuclear polyoxomolybdate clusters published over the last 10 years are generalised. The bibliography includes 95 references.

I. Introduction

Polyoxometallate compounds formed by d elements of Groups V and VI of the Periodic Table have been attracting the rapt attention of researchers for many years.[1] The interest in these substances is related first of all to the possibility of using them as efficient catalysts, biologically active compounds or new analytical reagents.[1,2] Polyoxometallate complexes often form unique supramolecular ensembles which possess unusual magnetic or spectral properties. For the preparation and practical application of such systems, reliable and efficient methods for the synthesis of polyoxometallates are needed first of all. It is very important to find approaches to the chemical design of clusters containing open shell metal centres,[3–7] because these systems are expected to form structures possessing unusual electronic characteristics.[8] It has been suggested that these polyoxometallates can be regarded as representing a new class of inorganic compounds whose chemical activity can be deliberately controlled. This is due to the exceptionally high reactivity of their molecules with respect to various reagents due to the presence of metal centres of different electronic nature.[1,9]

Some (giant) polyoxomolybdate clusters can be used to perform the design and deliberate engineering of materials with desired properties.[10] For instance, some polyoxometallates can be employed to model n-type semiconductor oxides.[1] Meanwhile, the capability of binding to one another discovered for giant polyoxomolybdate ring-shaped clusters containing nano-sized cavities opens up prospects for the design of unusual polymeric materials.[11] The possibility of introducing magnetically active centres into polyoxometallates makes these compounds promising for the preparation of molecular magnets — magnetic materials of a new generation. All these facts stimulate studies along these lines; nevertheless, development of target-directed synthesis of polynuclear compounds with a specified structure and elucidation of structure – properties relationships still remain among the most important problems.

II. Key principles of the formation of polyoxometallate clusters

Modern inorganic chemistry often deals with large structured systems. The routes for their formation are usually analysed by means of a fairly versatile strategy that has proved to be efficient. According to this strategy, an object is split (at least, hypothetically) into elementary fragments called building blocks (polygons, polyhedra, aggregates composed of such blocks, *etc.*) and then the rules of interaction and mutual binding of these blocks are studied.[12] Such a strategy is used in this review to consider large polyoxometallate clusters.

The ability of elementary building blocks and their derivatives to be linked to one another in different modes is important in many fields of synthetic chemistry, especially in polyoxometallate chemistry. This permits the synthesis of a variety of compounds including those with nano-size properties. Of interest from this standpoint are anionic species composed of building blocks of the $\{MO_x\}$ type where M are d elements in high oxidation states.[1,2,9]

In Nature, complex molecules are often formed stepwise, either under conditions of genetic control or in self-assembly processes under dissipative conditions far from equilibrium. Such complex compounds are normally synthesised using a sequence of several reactions, which often proceed over very long periods of time. During these reactions, functional groups are manipulated to form covalent bonds one after another. Modern knowledge in the field of polyoxometallate chemistry allows the use of self-assembly processes in which fragments formed from simple starting compounds can be linked to each other to form various mesoscopic structures (with linear dimensions of several tens

S S Talismanov, I L Eremenko N S Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninsky prosp. 31, 119991 Moscow, Russian Federation. Fax (7-095) 954 12 79.
E-mail: stal@igic.ras.ru (S S Talismanov)
Tel. (7-095) 952 21 12, (7-095) 955 48 35. E-mail: ilerem@igic.ras.ru (I L Eremenko)

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† Dedicated to Professor Achim Müller, who has greatly contributed to the development of inorganic chemistry, on the occasion of his 65th birthday.

angstrom or more) and can further form macroscopic substances with network structures.[13, 14]

The structural principle of the assembly of polyoxovanadates, -molybdates and -tungstates is the same, in particular, in all structures, each metal atom forms a $\{MO_x\}$ coordination polyhedron mainly due to the M–O π-bonding, and these polyhedra, in turn, form the vertices of structural surfaces.[12] Nevertheless, more detailed examination of these unique objects reveals substantial differences depending on the metal atom incorporated in the structure.

The structure of almost any of the very large polyoxotungstate anions, unlike those of vanadates and molybdates, can be represented as being composed of subunits based on defect (lacunary) fragments of the Keggin ion [containing groups of the $\{W_3^{VI}O_{13}\}$ type] or its isomers. This can be explained, in principle, by high stability of such fragments, which is apparently due to the presence of very weak (but not negligible) W–W interactions in the $\{W_3\}$ triangles.[1] A significant feature of polyoxovanadates is the existence of different base types of polyhedra: $\{VO_4\}$, $\{VO_5\}$, $\{VO_6\}$. The pyramidal $\{O=VO_4\}$ fragments tend to form cluster shells topologically similar to fullerenes or V_2O_5 layers.[13, 14]

Most of the very large mixed-valence molybdates can be represented as structures consisting of the same or similar fragments — the $\{Mo_8\}$ or $\{Mo_{17}\}$ building blocks, which can be linked in different modes directly to one another or *via* some coordinating centres. Numerous growth processes that conform to these rules have been discovered; they result in the formation of giant ring-shaped, spherical or other systems containing 102, 132, 154, 176 and even 368 molybdenum atoms.[15] The classical $\{Mo_3O_{13}\}$ fragment is much less significant and exhibits a much lower tendency for participation in the subsequent assembly of the cluster (at least, in the case of reduced systems) compared to analogous tungstate systems.

Since the chemical behaviours of polyoxometallates derived from different elements are fairly different, the minimum number of metal atoms that allows the cluster to be regarded as large is not the same for vanadates, molybdates and tungstates ($n \geqslant 19$ for V_n; $n \geqslant 24$ for Mo_n; and $n \geqslant 20$ for W_n).[12]

This brings about an important question: whether it is possible to assemble even larger molecular structures, for example, clusters of a mesoscopic size. It should be borne in mind that real processes involve binding of a very large number of base fragments. The self-assembly of the tobacco mosaic virus consisting of a large number of pre-organised fragments can serve as an impressive example (see Section VI.1).[16]

Undoubtedly, a useful strategy for the formation of giant systems is to create rather large intermediates that could be easily connected in self-assembly processes; in particular, this can involve various cationic metal centres.[1, 12, 17] Indeed, quasi-pre-organised building blocks present in the solution can be linked to each other either directly or *via* some cations to give giant compounds.[18] At this stage, it is very important to have comprehensive information about the system. The key factor is to preserve high solubility of the intermediates (for example, due to a substantial negative charge), which is necessary to avoid uncontrolled binding and/or too early precipitation. This approach can be illustrated in relation to the replacement of metal centres with a high positive charge by formally less positive centres, in particular, replacement of Mo^{VI} atoms by V^{IV} atoms in the α-Keggin anions $[Mo_{12}XO_{40}]^{3-}$ (X = P, As). This process gives rise to anionic intermediates with a high negative charge (nucleophiles), which can be either merely stabilised by electrophilic centres or linked by means of these centres to form markedly bigger systems.[19–21] For instance, during the substitution of vanadium for molybdenum in the $[Mo_{12}AsO_{40}]^{3-}$ cluster, the arising intermediates $\{Mo_8^{VI}V_4^{IV}As^{V}O_{40}\}^{11-}$ can be stabilised, for example, by As^{III} centres to give the $[As_2^{III}Mo_8^{VI}V_4^{IV}As^{V}O_{40}]^{5-}$ cluster. In the absence of As^{III} and in the presence of NH_2OH as a reducing agent, further condensation takes place.[19, 21] Finally, the $\{Mo_{17}\}$ fragments formed as reactive intermediates can be linked in different ways by cations or cationic groups (VO^{2+}, Fe^{III}, MoO_2^{2+}) to form bigger molecular structures.

According to an empirical rule,[12] if the size of the polyoxometallate anion increases, this anion can participate in further growth processes as a soluble and non-hydrolysable particle only provided that its electron density remains virtually constant (which implies an increase in the overall charge). However, in some cases, the solubility is determined by other factors, for example, the presence of a very large number of coordinated water molecules. The isolation of several giant ring-shaped polyoxomolybdate clusters containing more than 150 molybdenum atoms and anions with low or very low charges can be considered as evidence supporting this statement.[22]

To summarise the foregoing, we will list the conditions favourable for the formation of large molecular complex systems from polyoxometallate building blocks in the course of a single reaction (without complicated multistage processes).[23]

1. The presence of linkable fragments, *i.e.*, building blocks.
2. The possibility of generating fragments with high values of free enthalpy to initiate polymerisation or growth processes accompanied, for example, by evolution of H_2O molecules.
3. The ready possibility of changing the structure of the building blocks.
4. The possibility of introducing heteroatoms into the fragment blocks.
5. The possibility of forming larger fragment blocks suitable for linking in different ways.
6. Neither too weak nor too strong binding between the fragments.
7. The possibility of controlling structurisation processes by templates.
8. The possibility of forming structural defects, for example, lacunary structures, in reaction intermediates.
9. The presence of low-lying unoccupied molecular orbitals in the fragments.
10. The possibility of electron density localisation and delocalisation.
11. The opportunity to control and change the charge, for example, by protonation, electron transfer reactions or by replacement of some fragments.

In principle, by selecting and creating particular conditions, one can synthesise molecular systems comparable in size even with proteins.

III. Formation of cluster anions containing $\{Mo_{17}\}$ fragments

The fragment containing 17 molybdenum atoms ($\{Mo_{17}\}$) is one of the most frequently encountered building blocks incorporated in polyoxomolybdate clusters. This fragment can be found in the $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ cluster anion (**1a**) (produced upon acidification of an aqueous solution of sodium molybdate with hydrochloric or nitric acid at a 36 : 64 molar ratio) and the $[Mo_{36}(NO)_4O_{108}(H_2O)_{16}]^{12-}$ cluster anion (**1b**) [formed upon the reduction of aqueous solutions of molybdates(VI) with hydroxylamine].[21, 24–30]

It is noteworthy that the structures of both cluster anions formally include a large number of diverse coordination polyhedra (Fig. 1, see p. 559), namely, two $\{MoO_6\}$, four $\{(O=)MoO_4(H_2O)\}$, eight $\{(O=)_2MoO_3(H_2O)\}$, eight $\{(O=)MoO_5\}$ and two $\{(O=)_2MoO_4\}$ octahedra; four $\{Mo(X)O_6\}$ pentagonal bipyramids [X = O (**1a**), NO (**1b**)] and four $\{Mo_2O_8(\mu\text{-}O)(\mu\text{-}H_2O)\}$ fragments consisting of two octahedra sharing an edge. Anion **1b** contains two fairly large fragments, $\{Mo_{15}^{VI}(MoNO)_2^{3+}O_{58}\cdot(H_2O)_2\}^{20-} \equiv \{Mo_{17}\}$, connected by two $\{MoO_2\}^{2+}$ groups in which two terminal oxygen atoms occupy *cis*-positions.

The $\{Mo_{17}\}$ fragments are composed, in turn, of two $\{Mo_8\}$ fragments linked through eight oxygen atoms and one molybdenum atom. The centres of these fragments are formed by

$\{MoXO_6\}$ pentagonal bipyramids, each of them being linked to five $\{MoO_6\}$ octahedra *via* edges; two of these octahedra are bound additionally to two more peripheral octahedra. The hypothetical replacement of the $\{MoNO\}^{3+}$ groups by $\{MoO\}^{4+}$ groups results in non-reduced anion **1a**. Similar $\{Mo_8\}$ fragments can also be found in the structures of molybdenum oxides, Mo_5O_{14} and $Mo_{17}O_{47}$ (see Ref. 31).

In anions **1a** and **1b**, the $\{Mo_{17}\}$ fragments are linked by two $\{MoO_2\}^{2+}$ centres to *cis*-arranged oxygen atoms. Cluster **1b** is stabilised due to double protonation of two bridging and four terminal oxygen atoms contained in two bridging and four terminal H_2O ligands, respectively. The presence of altogether four bridging H_2O ligands is an interesting structural feature of anion **1b** in which each of the four bridging water molecules belongs to one of four $\{Mo_2O_8(\mu\text{-}O)(\mu\text{-}H_2O)\}$ fragments and participates in the binding of two corresponding octahedra by sharing an edge.

By further reduction of the cluster anion $[Mo_{36}(NO)_4.O_{108}(H_2O)_{16}]^{12-}$ (**1b**) with excess hydroxylamine, it is possible to isolate a compound containing one-dimensional chains consisting of 38-nuclear cluster anions $[(H_2O)MoO_{2.5}\{Mo_{36}.(NO)_4O_{108}(H_2O)_{16}\}O_{2.5}Mo(H_2O)]^{12-}$ (**2a**) (here and below, letter '**a**' denotes the cluster anion derived from the corresponding compound).[32] Compound **2** can be represented as consisting of initial cluster anions **1b** attached to each other by neutral binuclear fragments, $\{(H_2O)O_2Mo^{V}OMo^{V}O_2(H_2O)\}$, which are shaped like two tetrahedra sharing a vertex. It is considered that not only some molybdenum(VI) ions (arising probably upon the destruction of some cluster anions **1b**) are reduced during the reaction to give binuclear $\{(H_2O)O_2Mo^{V}OMo^{V}O_2(H_2O)\}$ fragments but some molybdenum atoms in anions **1b** are also reduced with generation of active sites. These are the active sites that participate in the binding to the $\{(H_2O)O_2Mo^{V}OMo^{V}O_2(H_2O)\}$ fragments during further self-assembly and are finally oxidised by air oxygen.[32]

The presence of large $\{Mo_{17}\}$ fragments in type **1b** systems is a very important feature of these clusters. This opens up the possibility of generating larger systems by binding $\{Mo_{17}\}$ fragments as ligands with a high negative charge by various electrophilic groups. In the case of cluster **1b,** this function is performed by the $\{MoO_2\}^{2+}$ cations.

When other electrophiles such as Fe^{III} or V^{IV} are used in the preparation of cluster **1b**, this yields giant cluster anions with the $\{Mo_{57}M_6\}$ metal core. The synthesis can be carried out in two ways by using either compounds of heterometal M in higher oxidation states (Fe^{III}, V^{V}) in the presence of a reducing agent ($NH_2OH \cdot HCl$) or a reducing agent alone containing atoms of the heterometal in a lower oxidation state (Fe^{II}, V^{IV}).

The resulting highly symmetrical (D_{3h}) cluster anions $[\{V^{IV}(H_2O)O\}_6\{Mo^{V}(\mu\text{-}H_2O)_2(\mu\text{-}OH)Mo^{V}\}_3\cdot\{Mo^{VI}_{15}(MoNO)_2O_{58}.(H_2O)_2\}_3]^{21-} \equiv \{Mo_{57}V_6\}$ (**3a**)[21] and $[\{Fe^{III}(H_2O)_2\}_6\{Mo^{V}.(\mu\text{-}H_2O)_2(\mu\text{-}OH)Mo^{V}\}_3\{Mo^{VI}_{15}(MoNO)_2O_{58}(H_2O)_2\}_3]^{15-} \equiv \{Mo_{57}Fe_6\}$ (**4a**)[19] each contain 276 non-hydrogen atoms. They tend to form a variety of different coordination polyhedra. Each of these anions (Fig. 2, see p. 559) includes three MoO_6, six $(O=)MoO_4(H_2O)$, twenty four $(O=)MoO_5$, twelve $(O=)_2MoO_4$ and six $(O=)V(H_2O)O_4$ or $FeO_4(H_2O)_2$ octahedra, six $Mo(NO)O_6$ pentagonal bipyramids, as well as $O_3\{Mo^{V}(\mu\text{-}H_2O)_2(\mu\text{-}OH)Mo^{V}\}O_3$ fragments, which can be described as two octahedra sharing a face. These structures are formally composed of three above-noted large $\{Mo^{VI}_{15}(MoNO)^{3+}_2O_{58}(H_2O)_2\}^{20-} \equiv \{Mo_{17}\}$ fragments functioning as bridging ligands connecting six cationic centres $[\{(O=)VO_4\}^{2+}$ in anion **3a** and $\{FeO_4(H_2O)_2\}$ in anion **4a**] and three $\{Mo^{V}(\mu\text{-}H_2O)_2(\mu\text{-}OH)Mo^{V}\}^{9+}$ binuclear groups. Yet another important feature of structures **1b**, **3a** and **4a** is the presence of bridging H_2O ligands, six in anions **3a** and **4a** and four in anion **1b**. In clusters **3a** and **4a**, these ligands occupy bridging positions between neighbouring Mo^{V} centres, giving rise to three $\{Mo^{V}(\mu\text{-}H_2O)_2(\mu\text{-}OH)Mo^{V}\}$ fragments, which can be described as two octahedra sharing a face. In anion **1b**, each of four bridging H_2O molecules belongs to one of four $\{Mo_2O_8(\mu\text{-}O)(\mu\text{-}H_2O)\}$ fragments, the corresponding octahedra sharing an edge.

The fairly large cavities inside these cluster anions are formally accessible, for example, to solvent molecules, owing to two 'holes' situated on the S_3 axis. These cavities whose diameter (without taking into account the hydrogen atoms) equals $\sim$0.9 nm in the direction normal to the S_3 axis and $\sim$0.5 nm in the direction parallel to the S_3 axis are formed by the central $\{O_{33}\}$ polyhedron. Two 'holes' are confined by two nearly planar 12-membered rings with the Mo–O–M–O fragments [M is V (**3a**) or Fe (**4a**)] in which metal atoms alternate.

One more important structural feature of these systems is the presence of three, rather large cavities between the $\{Mo_{17}\}$ fragments. These cavities are accessible for further coordination of highly electrophilic oxometallate fragments, for example, $\{MoO\}^{4+}$ (see Ref. 8) or $\{VO\}^{3+}$ (see Ref. 33), which results in discrete growth of such structures to give anions such as $\{Mo_{57+x}V_6\}$ and $\{Mo_{57}V_{6+x}\}$ ($x = 0-6$). Each $\{MoO\}^{4+}$ or $\{VO\}^{3+}$ group is bound to three oxygen atoms belonging to the $\{Mo_{57}V_6\}$ core; hence, the metal atoms in these groups exist in a tetrahedral environment. The degree of occupancy of the cavities can be brought in correlation with the degree of reduction of the initial cluster **3a**. The reduction of anion **3a** (Fig. 3, see p. 559) results in an increase in its nucleophilicity, thus initiating the growth, which may involve the insertion of up to six electrophilic centres, $\{MoO\}^{4+}$ or $\{VO\}^{3+}$, to give $[H_3Mo_{57}V_6(NO)_6.O_{189}(H_2O)_{12}(MoO)_6]^{21-}$ and $[H_3Mo_{57}V_6(NO)_6O_{189}(H_2O)_{12}.(VO)_6]^{15-}$ clusters, respectively.

Despite the fact that compounds **3** and **4** lose some water of crystallisation when stored in air, this does not influence their stability. According to IR spectroscopy data, they do not decompose up to a temperature of 225 °C. These compounds are also stable in aqueous solutions at pH 2.5–3.5 for several days. At lower or higher pH values, anions **3a** and **4a** decompose instantaneously, apparently, due to the electrophilic character of the NO group.

Note that by addition of various amounts of $FeCl_2 \cdot 4\,H_2O$ or $FeCl_3 \cdot 6\,H_2O$ to the reaction solution (crystallisation of which gives compound **3**), one can prepare a series of clusters with the same cluster core but with different statistical distribution of oxovanadium(IV), iron(II) and iron(III) centres among octahedral 'heterometallic' positions. Examples of compounds synthesised in this way are compounds with $\{Mo_{57}V_4Fe_2\}$, $\{Mo_{57}V_3Fe_3\}$, $\{Mo_{57}V_2Fe_4\}$ and $\{Mo_{57}VFe_5\}$ cluster anions containing iron(II) and iron(III) and the $\{Mo_{57}VFe^{III}_5\}$ cluster anion incorporating only iron(III) atoms. It should be noted that both the overall number of inserted iron atoms and the Fe^{II}/Fe^{III} ratio depend on the reaction conditions, in particular, on whether it was carried out in air or under an inert atmosphere.[34] This circumstance allows one to change the ratio of the number of vanadium centres to the number of iron centres (n_V/n_{Fe}) distributed over six positions, which form a trigonal prism inside the cluster, by varying experimental conditions. During the formation of a heterometallic cluster, only a small amount of $FeCl_3 \cdot 6\,H_2O$ is required for the insertion of iron into the giant cluster anion. However, when $FeCl_2 \cdot 4\,H_2O$ is used as the iron-containing component, a large excess of iron(II) chloride is needed to reach the same n_V/n_{Fe} ratio. Apparently, this outcome is related, according to the Pearson principle, to the higher reactivity of 'hard' iron(III) centres with respect to 'hard' acids (oxygen atoms), which are present in the coordination environment provided by the shell of the initial homomolybdenum cluster. Upon the addition of excess $FeCl_3 \cdot 6\,H_2O$, compound **4** can be isolated.

Magnetic properties of compounds of this type depend on both the overall content of iron and the Fe^{II}/Fe^{III} ratio. As expected, an increase in the iron content results in an increase in the magnetic susceptibility χ.[34] In the case of compounds containing both iron(II) and iron(III), the $\chi T(T)$ curve passes through a

maximum in the field of low temperatures, this maximum being more pronounced for clusters with high contents of iron. Although full analysis of the magnetic parameters for such systems is as yet rather difficult, this type of $\chi T(T)$ dependence is usually observed for ferrimagnetic systems. As the iron content decreases, the χT decreases and the ferrimagnetic properties become less pronounced. In the limiting case, where no iron is involved (*e.g.*, in $\{Mo_{57}V_6\}$), as for the intermediate compound (in $\{Mo_{57}V_4Fe_2\}$), the system follows an antiferromagnetic type of behaviour. It is noteworthy that the insertion of iron(II) enhances the ferrimagnetic properties, while the $\chi T(T)$ curve for $\{Mo_{57}VFe_5^{III}\}$, unlike that for $\{Mo_{57}VFe_5\}$, does not exhibit a maximum typical of ferrimagnetics. Müller *et al.*[34] believe that the pattern of the $\chi T(T)$ curves, especially in the case of ferrimagnetic systems, can be interpreted only by assuming the presence of different paramagnetic centres in the same cluster anion (rather than in different anions with the same average ratio of the numbers of such centres over all anions).

These data may suggest that deliberate variation of the electronic state of heterometallic centres would allow one to control the magnetic properties of the synthesised clusters.

The compound $(NH_4)_{21}[Mo_{45}^{VI}Mo_6^{V}(MoNO)_6Cu_2^{II}V_4^{IV}O_{178}\cdot(OH)_3(H_2O)_{16}]\cdot 60\,H_2O$ (**5**), containing three sorts of metal atoms — molybdenum, copper and vanadium,[35] is produced in the reaction of the $(NH_4)_{12}[Mo_{36}(NO)_4O_{108}(H_2O)_{16}]\cdot 33\,H_2O$ cluster (**A**) with excess $Cu^{I}Cl$ on heating in water at 60 °C with subsequent addition of $VOSO_4$. The geometry of the corresponding cluster anion **5a** is similar to that observed for structures **3a**, **4a** except that in this anion, about two $\{Cu(H_2O)_{1.2}\}^{2+}$ centres (the corrected occupancy of positions is close to unity) and about four $\{V=O\}^{2+}$ centres are distributed statistically over six heterometallic positions. Since these centres are disordered, they cannot be distinguished by X-ray diffraction; however, according to elemental analysis, the V/Cu ratio is equal to 4 : 2. The binuclear linkers in anion **5a** are fully reduced, and their structure can be described as $\{Mo^{V}(\mu\text{-}H_2O)_2(\mu\text{-}OH)Mo^{V}\}^{9+}$.

Thus, the synthetic strategy chosen can be used to prepare giant cluster anions $\{Mo_{57}M_x^1M_{6-x}^2\}$ with metal atoms of different sorts, which is especially important as regards the development of multifunctional catalysts.

As noted above, the $\{Mo_{57}M_6\}$ type anions are formally assembled from different blocks and linkers. However, due to the presence of reactive fragments, they can themselves function as building 'superblocks' for the formation of supramolecular structures. For instance, the reaction of cluster **A** with excess $FeCl_2\cdot 4\,H_2O$ on heating in water (65 °C) gave the compound[36] $\{(NH_4)_{12}[Mo_{45}^{VI}Mo_6^{V}(MoNO)_6Fe_6^{III}Fe_{1.5}^{II}(OH)_3(H_2O)_{30}]\cdot 64\,H_2O\}_n$ (**6**), containing a $\{Mo_{57}Fe_6^{III}\}^{12-}$ type cluster anion (**6a**), which is similar in structure to other clusters of this family considered above. Three large $\{Mo_{17}\}$ building blocks are linked to each other by three binuclear $\{Mo^{V}(\mu\text{-}H_2O)_2(\mu\text{-}OH)Mo^{V}\}^{9+}$ fragments and six octahedral $\{Fe(H_2O)_2\}^{3+}$ centres. However, the structure of **6** has a significant distinction from the structures of **3**–**5** (Fig. 4), namely, the crystal contains additional $\{Fe(H_2O)_4\}^{2+}$ centres in 12 symmetrically equivalent positions, the degree of occupancy of each of them being 25% (which corresponds to 1.5 Fe^{II} centres per one cluster anion). The ^{57}Fe Mössbauer spectrum of compound **6** recorded at 150 K contains two doublets, $\delta_1 = 0.48/\Delta E_1 = 1.10$ (typical values for $Fe^{III}O_6$) equal to 80%; $\delta_2 = 1.29/\Delta E_2 = 3.13$ (typical values for $Fe^{II}O_6$) equal to 20% (δ_i is the position of the line centre, ΔE is splitting). The Fe^{III}/Fe^{II} ratio according to Mössbauer spectroscopy is also equal to $6/1.5 = 4$. These additional metal centres play a role of linking fragments between the clusters; they form a planar network structure in which any two neighbouring cluster anions are bound according to the $Mo-O-Fe^{II}-O-Mo$ pattern (see Fig. 4).

Compound **6** is the first example of polymeric anionic networks formed by the $\{Mo_{57}M_6\}$ cluster blocks. The principle of formation of this structure can be clearly followed: first, the $\{Mo_{17}\}$ fragments are connected by $\{Fe(H_2O)_2\}^{3+}$ linkers to form cluster anions of the $\{Mo_{57}Fe_6^{III}\}$ type, while the resulting fragments are connected by the $\{Fe(H_2O)_4\}^{2+}$ linkers to form a cross-linked network. Finally, the chemical and physical properties of this compound are determined by a diversity of metal centres in different oxidation states (Mo^{VI}, Mo^{V}, Fe^{III}, Fe^{II}). Its electronic structure may be favourable for the temperature-dependent transfer of electrons in anion **6a**.[37,38]

IV. Interconversions of some polyoxomolybdates in organic solvents

Whereas studies dealing with the chemistry of water-soluble polyoxomolybdates carried out in recent years revealed a great number of diverse structures containing giant cluster anions including mixed-valence and heterometallic ones (see, for example, Refs 12, 23), the chemistry of polyoxomolybdates in solutions in organic solvents has been much less studied. The studies mainly dealt with modification of the known polyoxometallate systems such as the $[Mo_6^{VI}O_{19}]^{2-}$ anion (Lindqvist's structure)[39] by various functional groups, resulting in nitrosyl, diazenide, hydrazide, cyclopentadienyl and diazoalkane derivatives.[40–47] The conditions and ways of generation, and, what is most important, the interconversions of unsubstituted polyoxomolybdates in organic solvents have been little studied. The relevant data are described systematically in a publication.[48]

The exchange reaction of ammonium heptamolybdate $(NH_4)_6Mo_7O_{24}\cdot 4\,H_2O$ with tetrabutylammonium halides gives, after recrystallisation of the precipitated white solid from acetonitrile, colourless crystals of $(NBu_4^n)_4[Mo_8O_{26}]\cdot 4\,MeCN$ (**7**). According to X-ray diffraction data (Fig. 5), the octanuclear cluster anion $[Mo_8(\mu_3\text{-}O)_6(\mu_2\text{-}O)_6O_{14}]^{4-} \equiv [Mo_8O_{26}]^{4-}$ (**7a**) present in this compound contains six Mo^{VI} atoms in an octahedral environment and two Mo^{VI} atoms in a tetrahedral environment. Each molybdenum atom in the octahedral environment is connected to two terminal, two μ_2-bridging and two μ_3-bridging oxygen atoms, while each molybdenum atom in the tetrahedral environment is linked to one terminal and three μ_3-bridging oxygen atoms. In the polyhedral representation, anion **7a** can be regarded as an assembly formed by a ring composed of six MoO_6 octahedra, any of which shares two edges with two neighbouring octahedra. This gives rise to a ring closed on two sides by two MoO_4 tetrahedra, which are rotated through 60 ° relative to each other. The solvation acetonitrile molecules occupy the voids between the tetrabutylammonium cations and the cluster anions.

The reaction of cluster **A** with NBu_4^nX (X = Cl, Br, I, ClO_4) in an aqueous solution in air at room temperature followed by recrystallisation of the resulting beige-coloured precipitate from acetonitrile afforded yellow-coloured compound $(NBu_4^n)_2[Mo_6O_{19}]$ (**8**). The corresponding hexanuclear cluster anion $[Mo_6O_{19}]^{2-}$ (**8a**)[39] contains six Mo^{VI} atoms in a distorted octahedral environment.[48] Note that during this reaction, four $\{Mo^{II}(NO)\}^{3+}$ groups of cluster **1b** are oxidised, probably, by air oxygen to yield four $\{Mo^{VI}O\}^{4+}$ groups. Correspondingly, each 36-nuclear cluster anion **1b** decomposes to give six anions **8a** with the loss of 16 electrons. In cluster **8a**, each of the six molybdenum atoms (Fig. 6) is connected to one terminal, four μ_2-bridging and one μ_6-bridging oxygen atoms. In terms of the polyhedral representation, anion **8a** can be regarded as a structure consisting of six MoO_6 octahedra, each of them sharing four edges with four neighbouring octahedra and all six octahedra having one common vertex.

The composition of the products of decomposition of cluster **1b** on treatment with tetrabutylammonium salts depends appreciably on the reaction conditions.[48] When an aqueous solution of cluster **A** is refluxed in air for 40 min, its colour changes from red-brown to blue-green, while the addition of tetrabutylammonium halides gives rise to a blue-green precipitate. Recrystallisation of this product from acetonitrile in air affords the crystals of octanuclear cluster **7**.

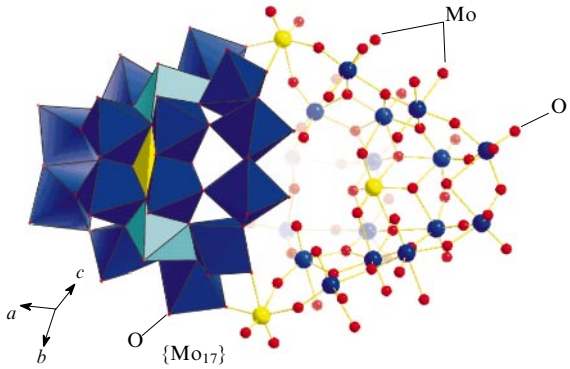


Figure 1. Structure of anions **1a** and **1b.** One $\{Mo_{17}\}$ fragment is shown in the polyhedral representation and the other is in the atomic representation.
The turquoise-coloured pentagonal bipyramids are the $\{Mo(X)O_6\}$ fragments, the yellow octahedron is the $\{MoO_6\}$ fragment, and blue octahedra are the other fragments; yellow spheres are the molybdenum atoms in the $\{MoO_6\}$ and $\{(O=)_2MoO_4\}$ fragments and blue spheres are the other molybdenum atoms.

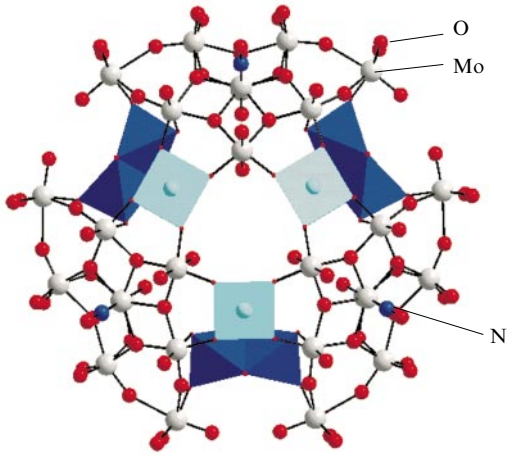


Figure 2. Structure of cluster anions **3a** and **4a**.
In the polyhedral representation, heterometallic centres (turquoise-coloured polyhedra) and binuclear linking groups (blue polyhedra) are shown.

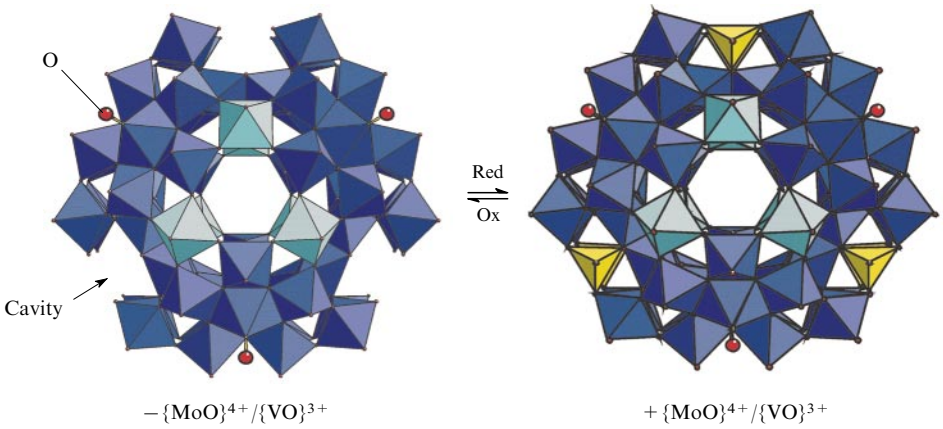


Figure 3. Molecular growth of clusters of the $\{Mo_{57}M_6\}$ family with filling of outer cavities.[8]
The turquoise-coloured polyhedra are heterometallic fragments; blue polyhedra are fragments formed by molybdenum atoms; yellow polyhedra are $\{MoO\}^{4+}/\{VO\}^{3+}$ fragments.

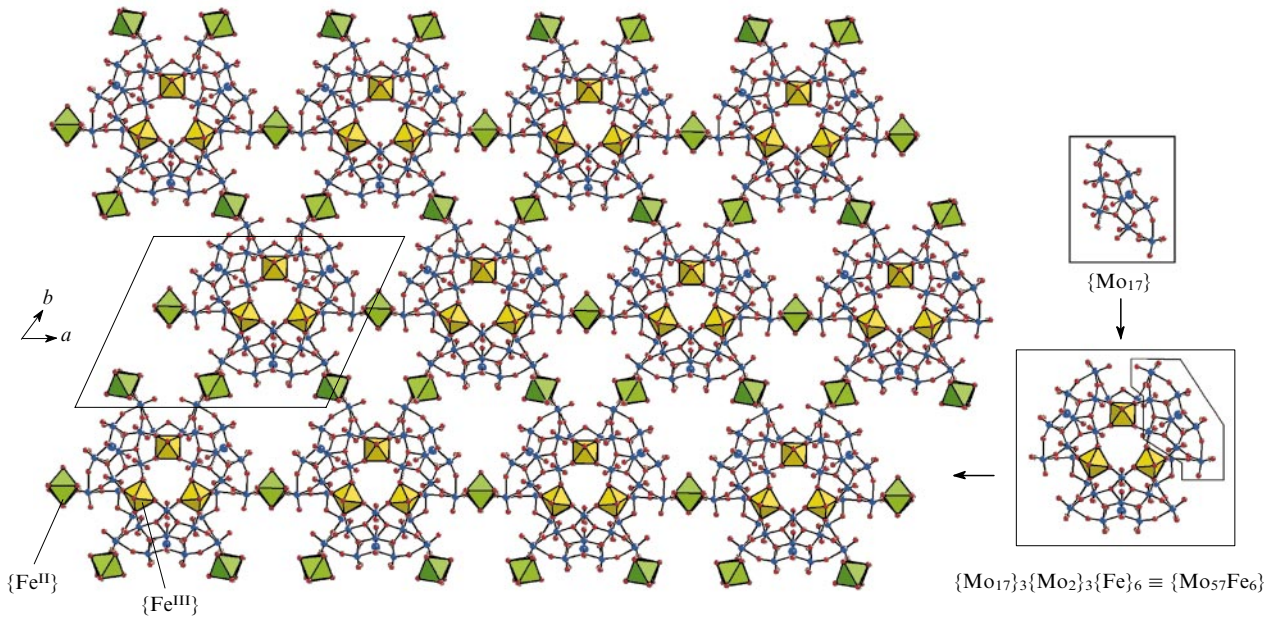


Figure 4. Network structure of cluster **6** and hierarchy of building blocks during its formation.

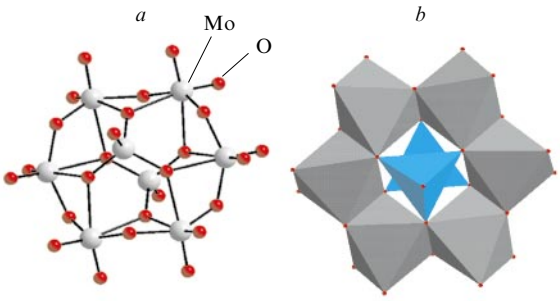


Figure 5. Structure of anion **7a** in the atomic (*a*) and polyhedral (*b*) representations.

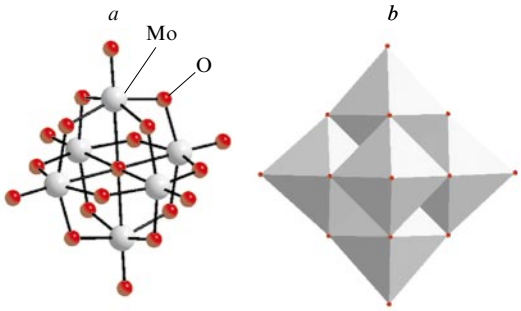


Figure 6. Structure of anion **8a** in the atomic (*a*) and polyhedral (*b*) representations.

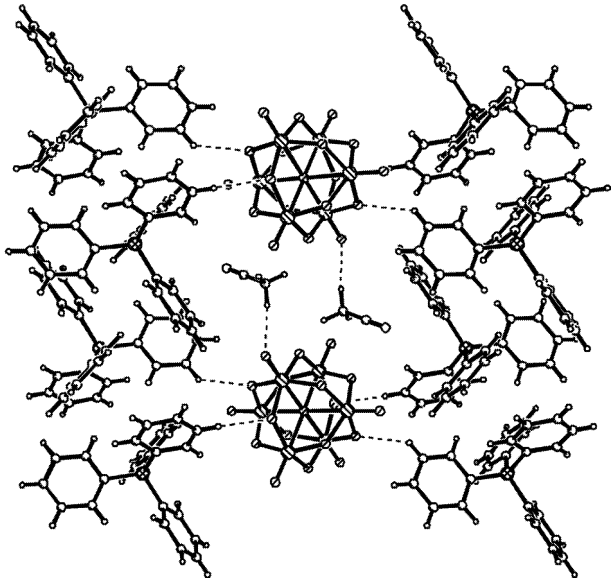


Figure 7. Fragment of the linear supramolecular structure of compound **9**.

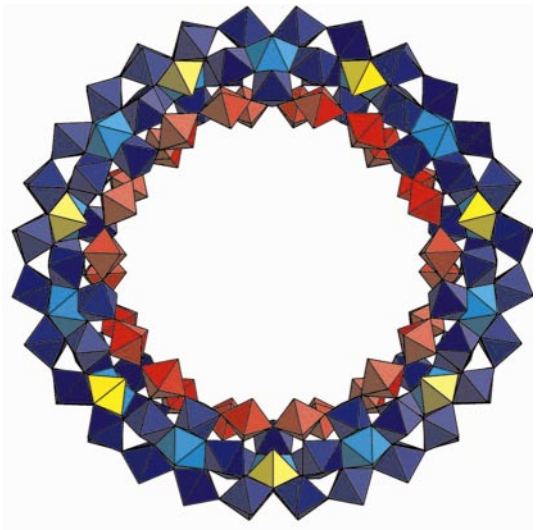


Figure 8. Structure of cluster anion **10a** in the polyhedral representation. Yellow octahedra are $\{Mo_1\}$ fragments, blue pentagonal bipyramids are the central $\{(O=)MoO_6\}$ parts of the $\{Mo_8\}$ fragments, red octahedra (in pairs) are $\{Mo_2\}$ fragments.

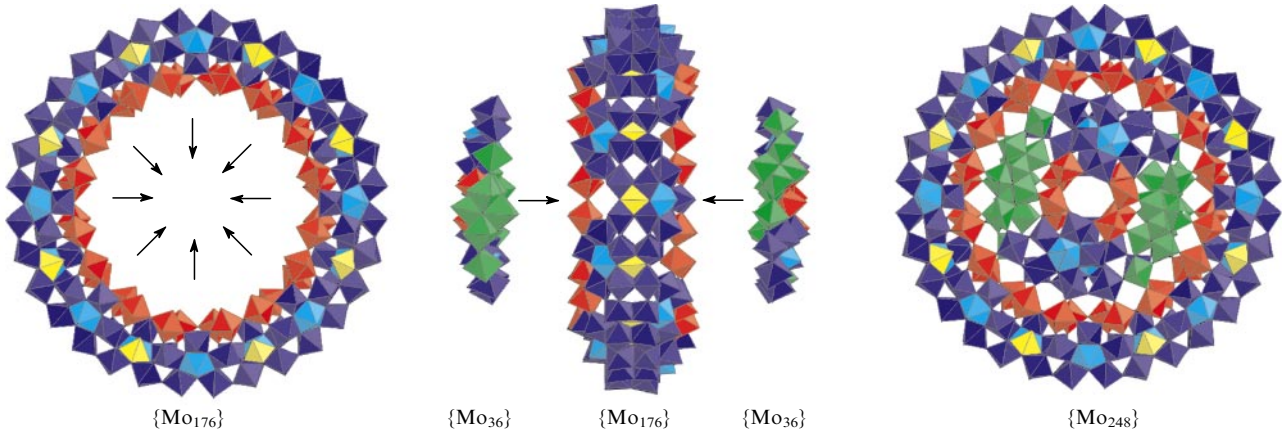


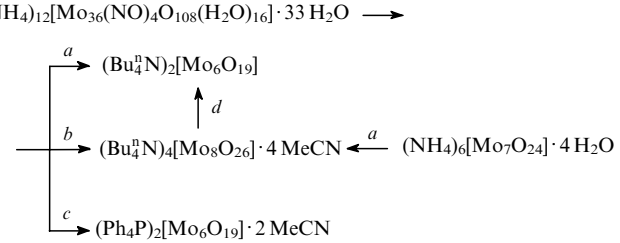
Figure 9. Structure of $\{Mo_{176}\}$ and $\{Mo_{248}\}$ cluster anions in the polyhedral representation and scheme of the molecular growth $\{Mo_{176}\} \rightarrow \{Mo_{248}\}$.[58] For designations of the polyhedra, see Fig. 8. The green colour marks fragments that cannot be represented in terms of fragments that constitute ring-shaped anions.

However, refluxing of compound **7** for several hours in a polar solvent such as acetone, acetonitrile or dimethyl sulfoxide induces cleavage of the octamer yielding hexanuclear cluster **8**.

Upon the heterogeneous reaction between cluster **A** in MeCN and Ph_4PCl (refluxing for 3 h), the cluster is completely converted into yellow-coloured compound $(Ph_4P)_2[Mo_6O_{19}] \cdot 2\,MeCN$ (**9**),[48] which also contains the hexanuclear cluster anion **8a**. The solva-

tion acetonitrile molecules occupy in the cell the voids between the cluster anions and form shortened contacts between the terminal oxygen atoms of the anions and the hydrogen atoms of the methyl groups. In addition, the presence of shortened contacts between the hydrogen atoms of the benzene rings of the cations and the μ_2 oxygen atoms of the anions is favourable for the formation of a complex supramolecular structure (Fig. 7).

The ways of controlling the structure of the resulting polyoxomolybdate anion by variation of the solvent and the reaction conditions during decomposition of cluster **A** have been summarised in a publication.[46] This procedure allows deliberate synthesis of octa- or hexanuclear polyoxometallate anions soluble in organic solvents in accordance with the following scheme:



(*a*) (1) Bu^n_4NX, H_2O, 20 °C, (2) MeCN; (*b*) (1) Bu^n_4NX, H_2O, 100 °C, (2) MeCN; (*c*) Ph_4PCl, MeCN, 82 °C; (*d*) refluxing in polar solvents.

V. Molybdenum blues

Solutions of molybdenum blues are formed almost instantaneously in the reduction of molybdenum(VI) compounds in acid media (pH $\leqslant$ 3). The suitable reducing agents include metals (Al, Pb, Mo, Cu, Zn, Cd, Hg), B_2H_6, $NaBH_4$, N_2H_4, NH_2OH, H_2S, SO_2, SO_3^{2-}, $S_2O_4^{2-}$, $S_2O_3^{2-}$, $SnCl_2$, $MoCl_5$, $MoOCl_5^{2-}$, formic acid, ethanol, ascorbic acid, thiourea, hydroquinone, D-glucose, saccharose, hydrogen or CO gas (under pressure). The blues can also be prepared by electroreduction, photochemical reduction or reduction induced by γ-radiation.[2,49]

The history of soluble molybdenum blues goes back to 1783 when a study by C W Scheele was published,[50] although blue waters from the springs of the Valley of Ten Thousand Smokes (Idaho) had been known much earlier. Berzelius was the first to propose the general formula for these compounds, namely, $Mo_5O_{14}\cdot n\,H_2O$.[51] Subsequently, researchers have used the formula MoO_x ($2.5 < x < 3$), as they have already believed that several types of molybdenum blues exist. Generations of chemists have attempted without success to crystallise these compounds in order to determine reliably their composition. The problem was in their very high solubility in water, which is now known to be due to the presence of numerous H_2O ligands. In recent years, this problem has been solved by A Müller and co-workers who used high concentrations of electrolytes to destroy the hydration shells. This allowed them to prepare single crystals of a large number of compounds containing giant ring-shaped anions of the $\{Mo_{154}\}$ (with and without defects) and $\{Mo_{176}\}$ types.[10,11,18,52–57] The formulae of some of them are given below:

(1) $(NH_4)_{28}[Mo_{154}(NO)_{14}O_{448}H_{14}(H_2O)_{70}]\cdot ca.\,350\,H_2O$ (discrete rings);

(2) $Na_{14}[Mo_{154}O_{462}H_{14}(MeOH)_8(H_2O)_{62}]\cdot ca.\,400\,H_2O$ (discrete rings);

(3) $Na_{26}[Mo_{142}O_{432}H_{14}(H_2O)_{58}]\cdot ca.\,300\,H_2O$ (discrete rings with defects);

(4) $\{Na_{24}[Mo_{144}O_{437}H_{14}(H_2O)_{56}]\cdot ca.\,250\,H_2O\}_n$ (chains of rings with defects);

(5) $\{Na_{16}[Mo_{152}O_{457}H_{14}(H_2O)_{66.5}]\cdot ca.\,300\,H_2O\}_m$ (layers of rings with defects).

It is worth mentioning that the first of these compounds, which contains the $[Mo_{154}(NO)_{14}O_{448}H_{14}(H_2O)_{70}]^{28-} \equiv \{Mo_{154}(NO)_{14}\}$ cluster anions (**10a**), can be prepared by acidification and reduction of solutions containing anions **1b**.[18] The giant ring-shaped anion **10a** (Fig. 8) consists of 140 $\{MoO_6\}$ octahedra and 14 $\{Mo(NO)O_6\}$ pentagonal bipyramids. The diameter of the central cavity in the equator is $\sim$20 Å. The anion **10a** (approximate D_{7d} symmetry) can be described as an assembly consisting of 14 subunits. Each subunit is an octanuclear fragment with the $\{Mo_8\}$ core whose centre is the $\{Mo(NO)O_6\}$ pentagonal bipyramid connected to seven $\{MoO_6\}$ octahedra through common vertices and edges. These $\{Mo_8\}$ fragments are situated above and below the equatorial plane of the cluster. Equivalent $\{Mo_8\}$ building blocks are also present in anions **1b**, **3a** and **4a** (see Section III). The key difference between two above-mentioned structural types (**1b**, **3a** and **4a**, on the one hand, and **10a** on the other hand) is that the $\{Mo_8\}$ fragments in clusters **1b**, **3a** and **4a** are arranged exactly one above another being separated by a reflection plane, whereas these fragments in anion **10a** are rotated relative to each other about a C_7 axis through an angle of 360°/14. Since in anions **3a** and **4a**, the pentagonal bipyramids of each fragment are connected to each other *via* one $\{Mo_1\}$ fragment located in the equatorial plane, the $\{Mo_{17}\}$ fragments can formally be regarded as 'pseudo-discrete'. Thus, they can be considered to be isolated transferable ligands linked through the $\{Fe^{III}(H_2O)_2\}^{3+}$ or $\{V^{IV}O(H_2O)\}^{2+}$ cationic groups or the $\{Mo^V(\mu\text{-}H_2O)_2(\mu\text{-}OH)Mo^V\}^{9+}$ groups. In contrast to this, the shift of the $\{Mo_8\}$ fragments with respect to one another in cluster **10a** means that linking of every two of these structural elements requires two equatorial $\{Mo_1\}$ fragments. Every two neighbouring $\{Mo_8\}$ fragments situated above and below the equatorial plane are linked additionally through the μ_3-O atom. In addition, every two neigbouring $\{Mo_8\}$ fragments located in one plane are linked by a $\{Mo^{VI}O_2(H_2O)(\mu\text{-}O)Mo^{VI}O_2(H_2O)\} \equiv \{Mo_2\}$ group. This gives rise to a ring-shaped structure; in terms of the building block concept, its formula can be written as $[\{Mo_2^{VI}O_5(H_2O)_2\}\{Mo_7Mo(NO)O_{25}(OH)_2(H_2O)_3Mo\}]_{14} \equiv [\{Mo_2\}\{Mo_8\}\{Mo_1\}]_{14}$.

As noted above, a series of similar ring-shaped anions containing no NO groups have been prepared in recent years. Among these, noteworthy is the ring-shaped $\{Mo_{176}\}$ cluster (**11a**),[54] which can be represented as consisting of sixteen $[\{Mo_2\}\{Mo_8\}\{Mo_1\}]$ sets instead of fourteen sets (as is observed for anion **10a** and its analogues). In another unusual cluster (which can be prepared by reduction of anion **10a** with ascorbic acid) containing 248 Mo atoms (**12a**),[58] the $\{Mo_{176}\}$ ring is capped from two sides by two neutral polyoxomolybdate fragments $\{Mo_{36}O_{96}(H_2O)_{24}\}$ (Fig. 9). Their structure is almost identical to the structure of the crystalline Mo_5O_{14} oxide.[59] On the one hand, this similarity opens up the way for simulating the crystal growth and especially nucleation processes that take place during the formation of metal oxides and, on the other hand, it allows one to mimic the pattern of organisation of metal centres in biological systems, in particular, for some types of biomineralisation.

Detailed investigation of a large number of diverse structures of molybdenum blues demonstrated that they all contain 14 (or 16 in the case of hexadecamers) $\{Mo_5O_6\}$ fragments and each of the fragments has two 4d electrons.[60]

By linking ring-shaped cluster anions including those containing defects (*i.e.*, missing $\{Mo_2\}$ groups), one can obtain a multitude of solid-state chain or layer structures.[56] The structures of some of these compounds incorporate nano-sized channels. In addition, it was demonstrated that $\{Mo_{154}\}$ type ring-shaped anions can form colloid particles with a hydrodynamic radius of $\sim$80 nm in organic solvents.

The ring-shaped clusters connected in chains can also act as hosts with respect to smaller polyoxometallate clusters, for example, $\{Mo_{36}\}$ type clusters (**1a**,**b**). In such supramolecular systems $\{Mo_{36} \subset Mo_{148}\}$,[23] the host and the guest (located exactly in the host cavity) are connected *via* 16 hydrogen bonds and four Na^+ cations arranged in the gap between the host and the guest (Fig. 10, see p. 563).

Thus, one can list the following most typical properties and potential applications of the polyoxomolybdate clusters belonging to the 'molybdenum blue' class.[22]

1. The presence of nano-sized cavities, which opens up broad opportunities for the formation of supramolecular architectures according to the host–guest principle.

2. High hydrophilicity of the surfaces due to the presence of a large number of H_2O ligands, which entails the formation of an unusually extended hydration shell (this accounts for the high solubility of these clusters).

3. The presence of surfaces with large areas, which is the reason for the high affinity of these clusters for adsorbents such as activated carbon or silk.

4. The possibility of formation of discrete structural defects on the outer surface of the cluster rings.

5. Linking of the ring-shaped blocks both during ageing of their solutions and during oriented crystallisation processes.

6. The possibility of introducing molecules onto various sections of the cluster surface by means of replacement of H_2O ligands (this is accompanied by successive changes in the properties of the cluster and especially of its surface) and study of the reactions between molecules placed into the cluster cavities.

7. Structural analogy between the fragments and the catalytically active metal oxides; this allows these clusters to be regarded as molecular models of some heterogeneous catalysts.

VI. Spherical systems (keplerates)

Although molecular systems, even fairly large ones, can, in principle, be obtained by a multistage synthesis, the construction of exceedingly big, giant molecular systems, including those with unusual structures having very high symmetry (similar to the structures of simple spherical viruses) and unusual properties requires different approaches.

For example, in order to construct giant spheres that resemble in size and structure spherical viruses having an icosahedral symmetry (C_5, C_3, C_2), it is necessary to select a reaction system in which pentagonal fragments capable of producing 12 icosahedron vertices upon linking should first be generated.

1. Spherical giant clusters with binuclear Mo^V–Mo^V linkers

In the case of polyoxomolybdates, the $\{(Mo)Mo_5\}$ pentagonal fragments mentioned above consist of the central MoO_7 bipyramid connected to five MoO_6 octahedra through shared edges. When the solution contains classical binuclear $\{Mo_2^VO_4\}^{2+}$ linkers (which are often formed in reduced molybdate solutions in the presence of bidentate ligands) [61] capable of connecting pentagonal fragments, an icosahedral molecular system is formed consisting of 12 pentagons and 30 binuclear linkers mentioned above. If acetate anions function as bridging ligands for the $[Mo_2^VO_4]^{2+}$ groups, this gives a spherical cluster with the composition $[Mo_{72}^{VI}Mo_{60}^{V}O_{372}(AcO)_{30}(H_2O)_{72}]^{42-} \equiv \{Mo_{132}\}$ (**13a**),[62] in which the positions of the central Mo atoms in the $\{(Mo)Mo_5\}$ fragments form 12 vertices, while the $[Mo_2^VO_4]^{2+}$ groups (with the metal–metal bond and with a Mo–Mo distance of $\sim$2.6 Å) form 30 edges of the icosahedron (Fig. 11). Thus, the formula of anion **13a** can be written as follows: $[\{(Mo)Mo_5O_{21}\cdot(H_2O)_6\}_{12}.\{Mo_2^VO_4\}(AcO)_{30}]^{42-}$. The salt $(NH_4)_{42}[Mo_{72}^{VI}Mo_{60}^{V}O_{372}.(AcO)_{30}(H_2O)_{72}]\cdot 300\,H_2O\cdot 10\,AcONH_4$ (**13**) crystallises in the space group *Fm*3 with a close cubic packing of the spherical anions. In the cluster molecule, all the 132 oxygen atoms of the terminal Mo=O groups are directed outside the giant spherical anion **13a**, while the *trans*-arranged H_2O ligands of all the 72 Mo^{VI} centres are directed toward the centre of this anion.

This molecular system with sixty MoO_6 subfragments belonging to twelve $\{(Mo)Mo_5\}$ pentagons is a topological model of spherical viruses, namely, the tobacco mosaic virus. This virus contains 60 identical protein subfragments (coded by only one gene) or, in other words, 12 pentagonal capsomers (morphological fragments). Each capsomer is composed of 5 protomers.[63]

When the acetate bridging ligands are replaced by formate ones, a guest system represented by a water cluster consisting of $\sim$60 H_2O molecules connected by hydrogen bonds is formed in the cluster anion cavity due to the decrease in the steric restrictions.[64]

The acetate bridging ligands can also be replaced either completely by phosphate or hypophosphite anions or partially by hydrosulfate anions. These groups enter the $[\{(Mo)Mo_5O_{21}.(H_2O)_6\}_{12}\{Mo_2^VO_4(H_2PO_2)\}_{30}]^{42-}$ (**14a**) and $[\{(Mo)Mo_5.O_{21}(H_2O)_6\}_{12}\{Mo_2^VO_4(HSO_4)\}_{18}\{Mo_2^VO_4(AcO)\}_{12}]^{42-}$ (**15a**) cluster anions, formed upon the addition of excess bidentate anions derived from the corresponding acids to freshly prepared solutions of salt **13**.[65]

The compound $Na_{46}[Mo_{66}^{VI}Mo_{50}^{V}O_{331}(AcO)_{30}(H_2O)_{56}]\cdot$ *ca.* $300\,H_2O$ (**16**) (space group $Pmn2_1$) isolated as a salt,[65] which contains giant basket-like cluster anions (Fig. 12), crystallises from solutions of anions **13a** containing Na^+ cations on keeping in air for a long period. The structure of the $[Mo_{66}^{VI}Mo_{50}^{V}O_{331}(AcO)_{30}(H_2O)_{56}]^{46-}$ anion (**16a**) can formally be obtained from structure **13a** by removing the $\{[(Mo)Mo_5](Mo_2^V)_5\} \equiv \{Mo_{16}\}$ fragment. The relative content of Mo^V centres in anion **16a** is lower than that in anion **13a**; therefore, the formation of cluster **16a** from **13a** can be regarded as partial oxidation.

Salt **16** is much more soluble in water than compound **13**, whose anion (**13a**) contains mainly terminal oxygen atoms as ligands on the surface of a closed sphere. This difference in solubility is due to the easy ingress of solvent (water) molecules inside the cluster anion **16a**, whose internal surface is hydrophilic due to the presence of a large number of H_2O ligands. Therefore, salt **16** crystallises only in the case where the equilibrium is appreciably shifted toward the formation of basket-like particles. The solution should always remain dilute in order to avoid crystallisation of compound **13**. If the reaction is carried out at high concentrations of sodium acetate (which induces salting-out due to destruction of the hydration shell) or even in the presence of NH_4^+ ions whose salts are less soluble (than sodium salts), salt **13** crystallises.

The knowledge of the structure of anion **16a** is important for understanding the processes of ligand replacement in cluster **13a**, resulting in the formation of anions **14a** and **15a**. In addition, the following facts should be taken into account.

1. Ligand exchange cannot occur through the 'molecular windows' present in anion **13a** on C_3 axes because these windows (formed by $\{Mo_9O_9\}$ rings) are too small for the anionic ligands.

2. Compounds **14** and **15** can be isolated if a substantial amount of spherical cluster anions remains in the reaction medium.

3. The exclusion of ligand exchange through the 'windows' suggests that either the ligands that approach the spherical anion **13a** induce its opening or that the closed spherical cluster anions exist in equilibrium with the corresponding basket-like cluster anions.

In terms of the latter assumption, one can explain the easy crystallisation (after the ligand exchange) of compounds **14** and **15** containing spherical cluster anions **14a** and **15a**. The reason is a lower hydrophilicity of their surfaces compared to that of the surface of cluster **16a.** They are much less soluble than the basket-like anions equilibrated with them. Yet another argument supporting the existence of such an equilibrium is the fact that compound **13** can be isolated from solutions of compound **16** and *vice versa*. This does not provide any grounds for suggesting that the $\{Mo_{16}\}$ fragment is stable in solutions.[65]

2. Spherical giant clusters with mononuclear linking fragments

Binding of pentagonal $\{(Mo)Mo_5\}$ fragments by fragments other than binuclear $\{Mo_2^VO_4L\}$ makes it possible to vary the dimensions and properties of the giant spherical clusters formed. For example, oxidation of the spherical anion **13a** with air oxygen at

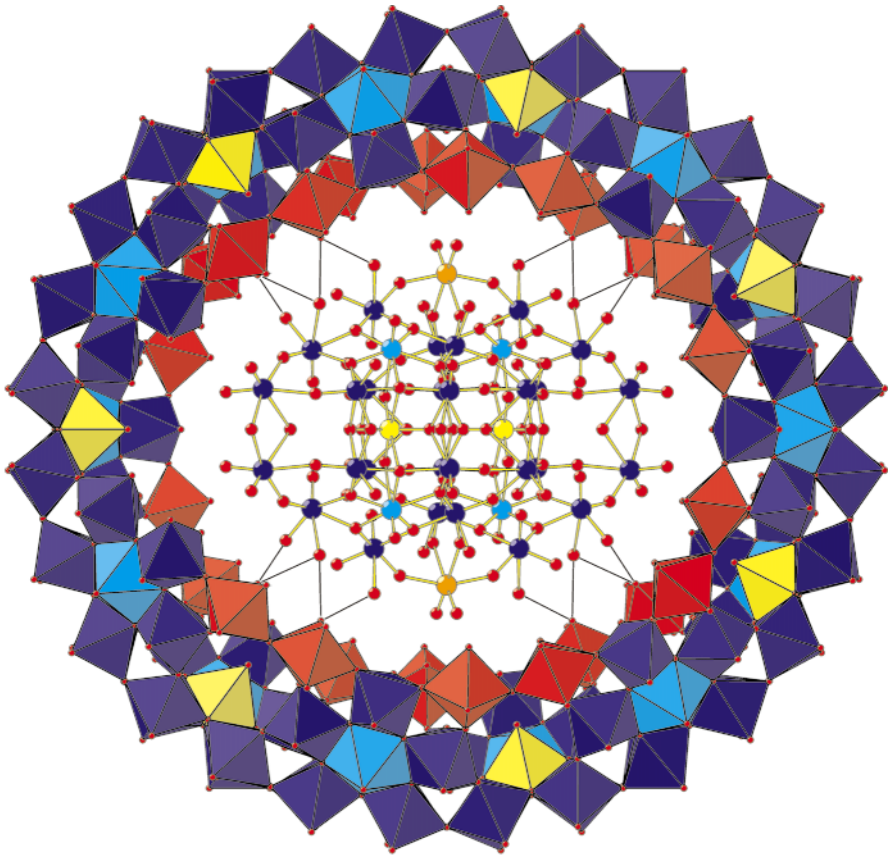


Figure 10. Structure of the $\{Mo_{36}\subset Mo_{148}\}$ supramolecular system. The $\{Mo_{148}\}$ cluster is given in the polyhedral representation and the $\{Mo_{36}\}$ cluster is in the atomic representation.[23]
For designations of the polyhedra, see Fig. 8.

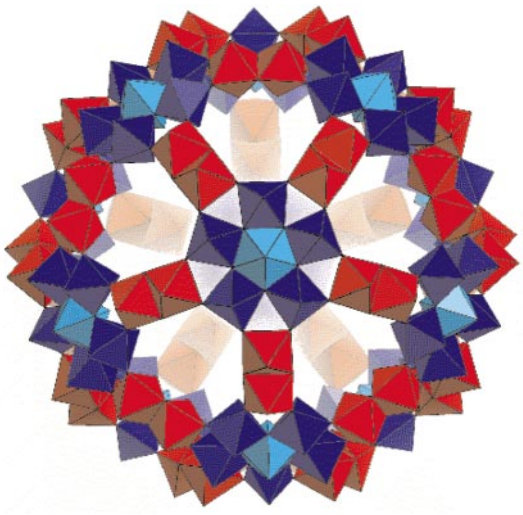


Figure 11. Structure of cluster anion **13a** in the polyhedral representation. Blue pentagonal bipyramids are the central parts MoO_7 of the $\{(Mo)Mo_5\}$ fragments; red octahedra (in pairs) are the $[Mo_2^{V}O_4]^{2+}$ fragments.

pH ~2.5 and at high NaCl concentrations gives rise to a dark-blue crystalline compound, $[\{(Mo)Mo_5O_{21}(H_2O)_6\}_{12}.\{Mo^{V}O(H_2O)\}_{30}]\cdot ca.\,150\,H_2O$ (**17**), containing neutral spherical cluster **17a** (Fig. 13). This product crystallises in the *C*2/*c* space group and, unlike cluster anion **13a** (the space group of salt **13** is *Fm*3), it does not form a close cubic packing. Like cluster anion **13a**, neutral cluster **17a** comprises 12 pentagonal fragments, $\{(Mo)Mo_5\}$, which are partially reduced (unlike those in anion **13a**). The pentagonal fragments in cluster **17a** are linked to one another by thirty $O=Mo^{V}(H_2O)$ fragments [the Mo=O bond length is ~1.67 Å; the Mo–O (*trans*-H_2O) distance is ~2.30 Å] to form an Archimedean solid, namely, icosidodecahedron. The Mo=O groups of the linkers are directed inside the sphere.[66]

In conformity with the Robin–Day classification, cluster **17a** can be defined as a mixed-valence compound of type II,[67] as indicated by its intensive dark blue colour. Of the 36 4d electrons belonging to molybdenum atoms (which are formally Mo^{V} centres determined by cerium redox titration), 30 electrons are mainly concentrated on the 30 molybdenum atoms that act as linkers, whereas the other six electrons are mainly delocalised among the molybdenum atoms of the pentagonal groups.

It is of interest that the EPR spectra of compound **17** measured at room temperature do not exhibit resonance signals in spite of the presence of a large number of unpaired electrons. Apparently, the absence of signals can be attributed to strong exchange interactions of the antiferromagnetic type.[66]

It should be noted that a structure with $Mo^{V}-Mo^{V}$ fragments (*i.e.*, with localised Mo–Mo bonds) does not exist in cluster **17a**, despite the fairly large number of Mo^{V} centres (formal). Local (partially) single-electron oxidative degradation of the $[Mo_2^{V}O_4]^{2+}$ linkers under mild conditions corresponds formally to the reaction $\{Mo_2^{V}\} \rightarrow \{Mo^{V}\} + Mo^{VI}$ followed by the formation of soluble polyoxomolybdates(VI). As this takes place, thirty Mo^{V} centers are trapped by a spherical matrix [twelve $\{(Mo)Mo_5\}$ pentagonal blocks], and their structure does not change. It is significant that this reaction involves the binding functional groups located on the surface of the giant sphere. This inevitably changes the dimensions of the molecule. Further

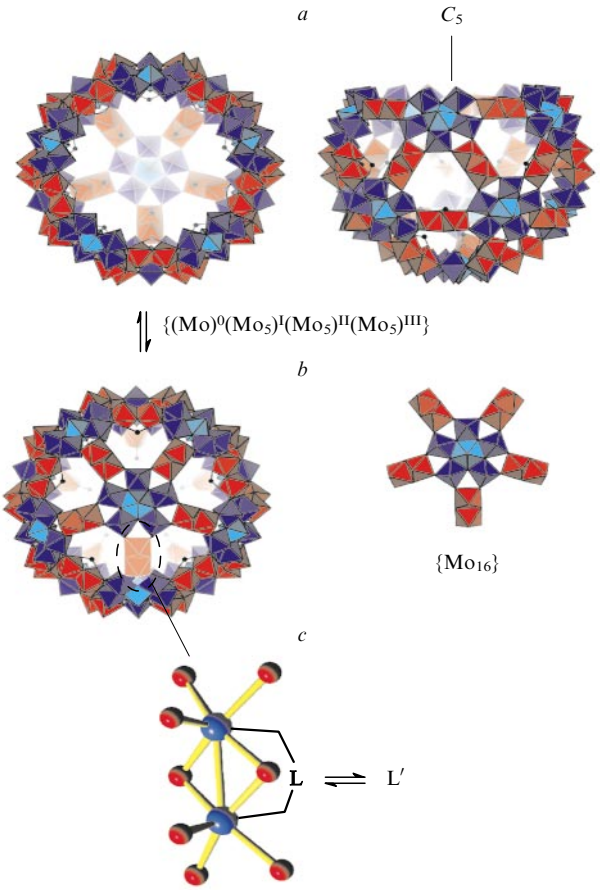


Figure 12. Structure of cluster anion **16a** in two projections in the polyhedral representation (*a*) and its formal difference from anion **13a** (*b*) (the {Mo$_{16}$} fragment is shown separately). Binuclear fragment {Mo$_2^V$O$_4$L} (*c*) in which the L $\rightleftharpoons$ L′ ligand exchange takes place.[65]

oxidation does not take place, as neutral cluster **17** has a low solubility and crystallises immediately after formation.

When a solution of salt **13** reacts with FeCl$_3\cdot$6 H$_2$O (pH $\sim$3) in the presence of ammonium acetate, the replacement of the {Mo$_2^V$} linkers in cluster **13a** by Fe^{III} centres gives rise to a yellow-coloured crystalline compound, [{(Mo)Mo$_5$O$_{21}$L$_6$}$_{12}${Fe^{III}(H$_2$O)L}$_{30}$]$\cdot$ *ca.* 150 H$_2$O (**18**),[68] where L is H$_2$O, AcO$^-$ or Mo$_2^{VI}$O$_{8/9}^{n-}$. Compound **18** contains 12 acetate ligands and three 'additional' Mo$_2$O$_{8/9}$ fragments (their total charge is -6). The structures of these fragments are given by {(μ-O)$_2$O=Mo^{VI}(OH)$_2$(H$_2$O)Mo^{VI}=O.(μ-O)$_2$}$^{2-}$ and {(μ-O)$_2$O=Mo^{VI}(H$_2$O)Mo^{VI}=O(μ-O)$_2$}$^{2-}$ with octahedral and square-bipyramidal coordination environments of the Mo atoms, respectively. These fragments are markedly disordered and function as tetradentate ligands inside the cluster shell. The twelve acetate ligands are also disordered, and their positions cannot be determined exactly, first of all, due to the large number ($\geqslant$120) of possible positions. It is evident that the hypothetical positively charged cluster formed upon substitution of the Fe^{III} centres for all linkers in anion **13a**, namely, [{(Mo)Mo$_5$O$_{21}$.(H$_2$O)$_6$}$_{12}${Fe^{III}(H$_2$O)$_2$}$_{30}$]$^{18+}$, would be exceptionally unstable under the reaction conditions. Thus, the formula of this compound can be written as [Mo$_{72}$Fe$_{30}$O$_{252}$(AcO)$_{12}${Mo$_2$O$_7$(H$_2$O)}$_2$.{H$_2$Mo$_2$O$_8$(H$_2$O)}(H$_2$O)$_{91}$]$\cdot$ *ca.* 150 H$_2$O.

Compound **18** crystallises in the space group *R*3 and contains discrete neutral spherical clusters **18a**. Each spherical cluster (see Fig. 13) consists of 12 pentagonal fragments of the {(Mo)Mo$_5$} type connected by 30 Fe^{III} centres; thus, the structure of **18a** has an approximate icosahedral symmetry and contains 102 metal atoms, and, in addition, their terminal ligands (O or H$_2$O) that belong to two concentric spheres. Each octahedron formed by a

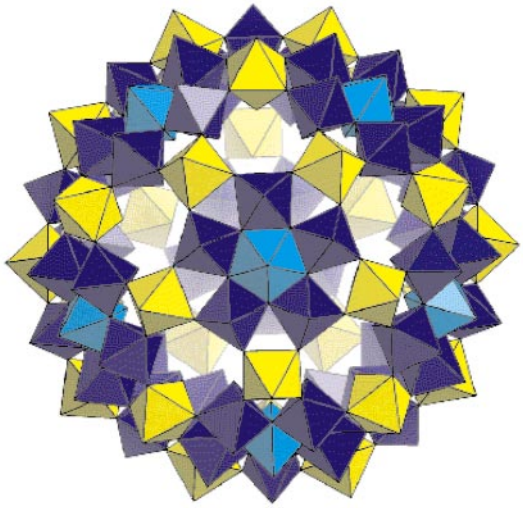


Figure 13. Structure of clusters [{(Mo)Mo$_5$O$_{21}$(H$_2$O)$_6$}$_{12}$.{Mo^{V}O(H$_2$O)}$_{30}$] (**17a**) and [{(Mo)Mo$_5$O$_{21}$L$_6$}$_{12}${Fe^{III}(H$_2$O)L}$_{30}$] (**18a**) in the polyhedral representation.
The yellow octahedra are the {Mo^{V}O(H$_2$O)}$^{3+}$ centres (in **17a**) or {Fe^{III}(H$_2$O)L}$^{3+}$ centres (in **18a**).

Fe^{III} centre is connected to two neighbouring pentagonal fragments. The midpoints of 12 pentagonal fragments, namely the Mo atoms in the MoO$_7$ pentagonal bipyramids, form an icosahedron, while thirty Fe^{III} centres form an icosidodecahedron.[69]

The Raman spectrum of compound **18** in a concentrated aqueous solution is virtually identical to the spectrum recorded for the solid. It should be noted that these solutions are acidic due to partial deprotonation of the H$_2$O ligands belonging to the Fe^{III} centres. The slight yellow colouring of the compound corresponds to the presence of polyoxomolybdate(VI) fragments and Fe^{III} centres. Magnetochemical measurements[70,71] indicate that cluster **18** contains high-spin Fe^{III} centres (the Fe^{III}–Fe^{III} distance is $\sim$6.4 Å), which are involved in rather weak antiferromagnetic exchange interactions described by the classical Heisenberg model.[70,71] The ^{57}Fe Mössbauer spectrum confirms the presence of only Fe^{III} centres in a slightly distorted octahedral oxygen environment.

The reaction of vanadyl sulfate with an acidified solution of sodium molybdate in the presence of high concentrations of an electrolyte (NaCl) gives the compound Na$_{20}$.[{Mo^{VI}O$_3\cdot$(H$_2$O)}$_{10}${V^{IV}O(H$_2$O)}$_{20}${(Mo^{VI})Mo$_5^{VI}$O$_{21}$(H$_2$O)$_3$}$_{10}$.({Mo^{VI}O$_2\cdot$(H$_2$O)$_2$}$_{5/2}$)$_2$({NaSO$_4$}$_5$)$_2$]$\cdot$170 H$_2$O (**19**).[72] The cluster anion [{Mo^{VI}O$_3$(H$_2$O)}$_{10}${V^{VI}O(H$_2$O)}$_{20}${(Mo^{VI}Mo$_5^{VI}$O$_{21}$.(H$_2$O)$_3$}$_{10}$({Mo^{VI}O$_2$(H$_2$O)$_2$}$_{5/2}$)({NaSO$_4$}$_5$)$_2$]$^{20-}$ (**19a**) present as a part of this structure is nearly spherical (its greatest and smallest outer diameters are equal to 25 and 23 Å, respectively) and has a C_5 symmetry axis (Figs 14, 15). The structure of this anion is best described as a distorted icosidodecahedron containing 20 triangular and 20 pentagonal faces, which are formed by 10 Mo^{VI} centres and 20 V^{IV} centres. Ten triangular faces composed of 20 V^{IV} centres form an unusual equatorial 'ring-shaped magnetic ribbon.' The other 10 triangular faces, each being formed by one V^{IV} centre and two Mo^{VI} centres, complete the distorted icosidodecahedron (see Fig. 14).

The cavity of cluster anion **19a** accommodates ten sulfate groups in a previously unknown mode [each group is connected to three neigbouring Mo^{VI} centres of each {(Mo^{VI})Mo$_5^{VI}$} group *via* three oxygen atoms] and ten Na$^+$ cations. The Na$^+$ cations are located between the neighbouring sulfate groups, which gives rise to two unusual {NaSO$_4$}$_5$ rings [the Na–O(SO$_3$) distance is 2.48–2.60 Å] lying above and below the equatorial ring composed of ten V^{IV} centres. Note that in this case, the Na ions possess a unique pentagonal-bipyramidal coordination environment. Five

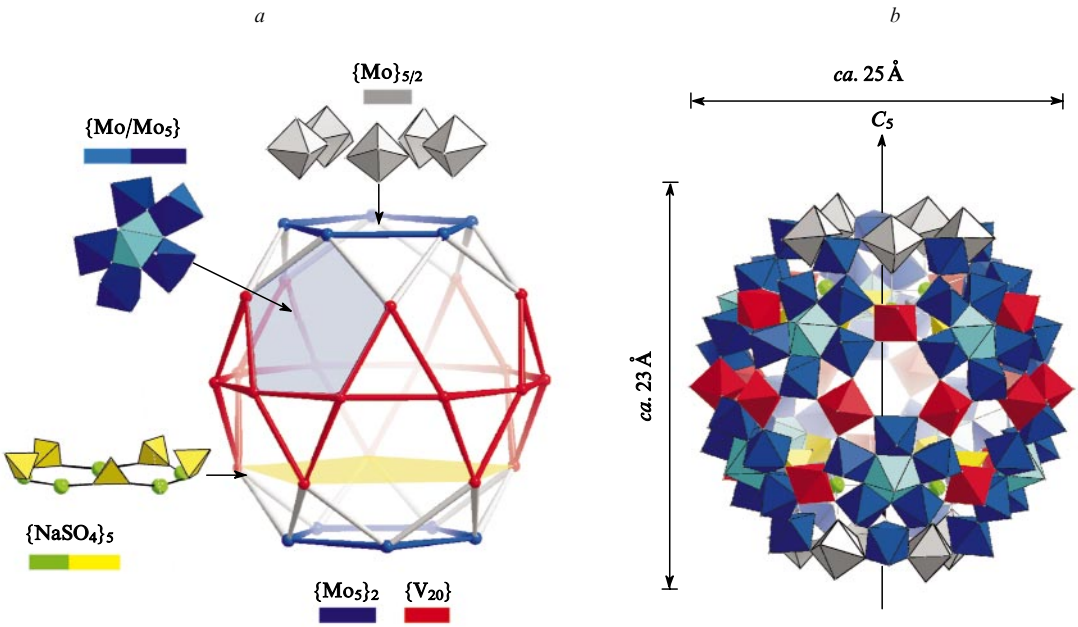


Figure 14. Structure of **19a** in the framework (distorted icosidodecahedron) (*a*) and polyhedral (*b*) representations.[72]

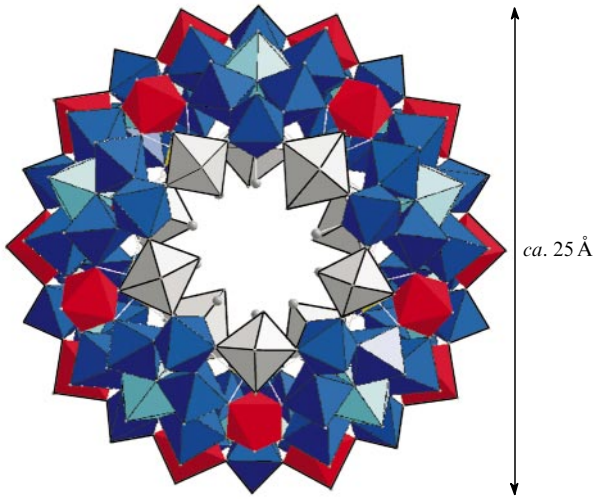


Figure 15. View of the structure **19** parallel to the C_5 axis in the polyhedral representation.[72]
For designations of the polyhedra, see Fig. 14.

of the seven corresponding oxygen centres belong to the cluster shell.

The measurements of the magnetic susceptibility of compound **19** showed a sharp decrease in the χT value in the range from 200 to 100 K (3.4–2.3 cm^3 K mol^{-1}), indicating the presence of strong antiferromagnetic exchange interactions despite rather long distances between the V^{IV} atoms (6.27–6.46 Å).

VII. Spherical giant clusters as building blocks in chemical design

The deliberate design of cross-linked structures having pre-specified properties from reliably characterised building blocks is among the most promising lines of research in modern inorganic chemistry.[73, 74] Thus linking of giant ring-shaped polyoxomolybdate clusters (see Section V) having open nano-sized cavities gives rise to two-dimensional networks.[11]

By varying the size of cluster anions (and, hence, their inner cavities) and by changing the nature of linkers on passing from anion **13a** to anion **18a**, one can create unusual chemical structures resulting from absolutely new reactions including insertion of a guest into the host cavity and/or cross-coupling of spherical clusters to form cross-linked polymeric structures. When a freshly prepared solution of salt **18** is acidified by hydrochloric acid to pH 2, the compound $[Mo_{72}Fe_{30}O_{252}(AcO)_{10}\{Mo_2O_7(H_2O)\}.\{H_2Mo_2O_8(H_2O)\}_3(H_2O)_{91}]\cdot 140\,H_2O$ (**20**) is formed; this product contains neutral spherical clusters $[Mo_{72}Fe_{30}O_{252}(AcO)_{10}.\{Mo_2O_7(H_2O)\}\{H_2Mo_2O_8(H_2O)\}_3(H_2O)_{91}]$ (**20a**), very similar to the cluster **18a**. The major difference between compounds **20a** and **18a** is the fact that the former has fewer acetate ligands and more binuclear oxomolybdate ligands. This can be sketched as follows:

$$\mathbf{18a} - 2\,AcO - [Mo_2^{VI}O_7(H_2O)]^{2-} + 2\,[H_2Mo_2^{VI}O_8(H_2O)]^{2-} = \mathbf{20a}.$$

However, even such minor changes in the structure of these clusters result in substantial changes in their reactivity: when dried in air at room temperature, compound **20a** undergoes solid-state condensation to give a cross-linked structure, $\{[H_4Mo_{72}Fe_{30}O_{254}(AcO)_{10}\{Mo_2O_7(H_2O)\}\{H_2Mo_2O_8(H_2O)\}_3\cdot(H_2O)_{87}]\cdot 80\,H_2O\}_n$ (**21**) (Fig. 16).[75] It is noteworthy that this process does not take place during drying of the crystals of **18a** with a different packing of cluster units. The clusters **20a** form the structure $[H_4Mo_{72}Fe_{30}O_{254}(AcO)_{10}\{Mo_2O_7(H_2O)\}\{H_2Mo_2O_8(H_2O)\}_3(H_2O)_{87}]$ (**21a**) *via* closure of Fe–O–Fe bridges between the neighbouring cluster units, which implies deprotonation of the H_2O ligands belonging to the iron atoms with subsequent condensation:

$$Fe(OH_2) + (H_2O)Fe \xrightarrow[-H^+]{} Fe(OH) + (H_2O)Fe \xrightarrow[-H^+,\,-H_2O]{} Fe-O-Fe.$$

In addition, the intermediate of this process $\{[Mo_{72}.Fe_{30}O_{252}(AcO)_{10}\{Mo_2O_7(H_2O)\}\{H_2Mo_2O_8(H_2O)\}_3(H_2O)_{91}]\cdot 100\,H_2O\}_n$ (**22**) was isolated as a single crystal and structurally characterised (so were both compounds described above). In compound **22**, close contacts occur between the $[Mo_{72}Fe_{30}O_{252}.(AcO)_{10}\{Mo_2O_7(H_2O)\}\{H_2Mo_2O_8(H_2O)\}_3(H_2O)_{91}]$ cluster units (**22a**); however, chemical bonds between them have not yet been formed.[75]

Since the reaction **20** → **22** → **21** takes place in the crystal at room temperature and mainly involves the transformation of giant spherical fragments, the crystal unit cells of the three compounds are fairly similar. Compounds **20** and **22** crystallise with a monoclinic space group $P2_1/n$ and have similar unit cell

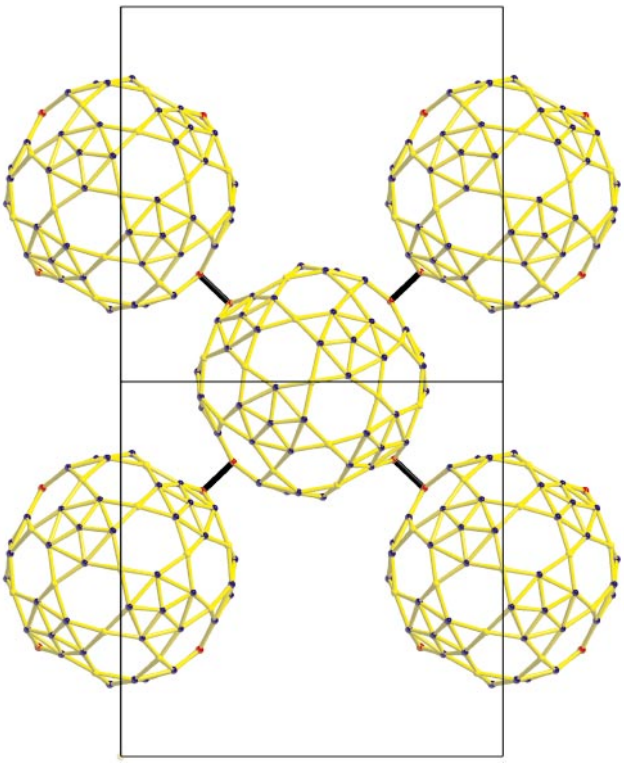


Figure 16. Structure of the metal core of the network structure of cluster **21a**.[75]
Blue spheres are molybdenum atoms; red and yellow spheres are iron atoms involved and not involved in the intersphere binding, respectively.

parameters and similar patterns of packing of the spherical clusters. During the condensation resulting in structure **21**, the clusters are re-oriented; consequently, the structure passes to a more symmetrical orthorhombic system (space group *Cmca*). The cluster re-orientation accompanied by the loss of crystal water mainly involves the translational shift of clusters towards one another with a very slight rotation. The shortest distance between the Fe^{III} centres of neighbouring spheres in structure **20** is 6.74 Å,

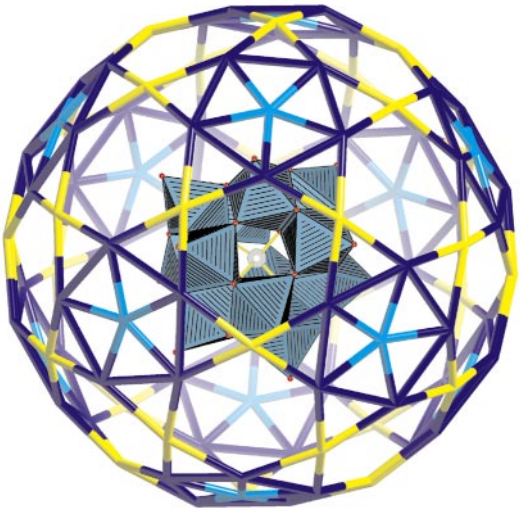


Figure 17. Structure of the cluster composite $[H_xPMo_{12}O_{40}\subset H_4Mo^{VI}_{72}\cdot Fe^{III}_{30}(AcO)_{12}O_{254}(H_2O)_{98}]$ (**23a**), a fragment of the layered structure **23**.[77]
For designations, see Figs 8, 13. The dashed polyhedra are encapsulated Keggin anions.

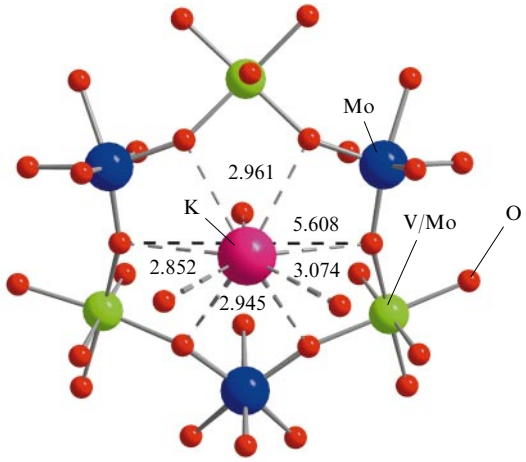


Figure 18. Interatomic distances in the $\{Mo_6O_6\}$ metal rings of the spherical polyoxomolybdate cluster with integrated K^+ cations.[84]

while this distance in cluster **22** amounts to 5.39 Å, and, finally, in structure **21**, the Fe–O–Fe distance is 3.79 Å. Magnetic measurements indicate that cluster **22** contains thirty Fe^{III} atoms, four of which are involved in strong exchange interactions of the antiferromagnetic type.

This process is analogous to classical inorganic condensation reactions, resulting in the formation of polycations;[76] however, unlike, for example, the hydrolysis of $[Fe(H_2O)_6]^{3+}$, this process is not chaotic.

Even more complex systems based on spherical clusters of the $\{Mo^{VI}_{72}Fe^{III}_{30}\}$ type can be synthesised in one step from simple reactants. Thus the addition of $FeCl_2\cdot 4\,H_2O$ in air to an acidic (pH 2) aqueous solution of polyoxomolybdate(VI) containing acetic acid and slight amounts of phosphate induces a complex self-assembling process giving rise to the neutral compound $\{[H_xPMo_{12}O_{40}\subset H_4Mo^{VI}_{72}Fe^{III}_{30}(AcO)_{12}O_{254}(H_2O)_{98}]\cdot 60\,H_2O\}_n$ (**23**), which is a novel type layered material (Fig. 17).[77,78] The building blocks that constitute this system are nano-sized oxometallate composites consisting of paramagnetic icosahedral

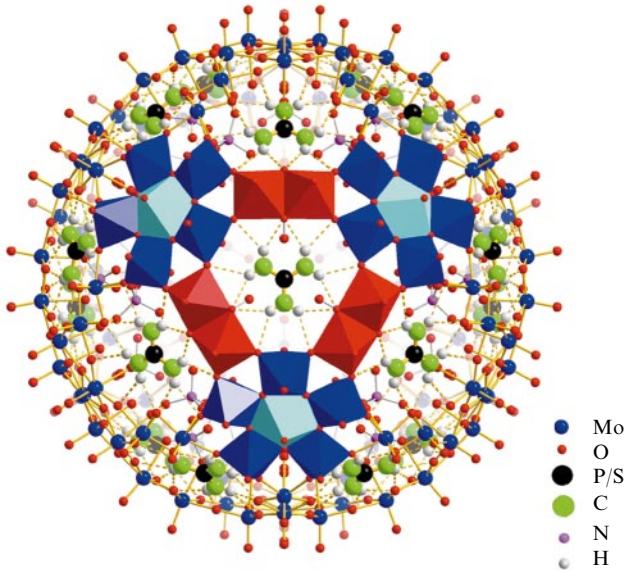


Figure 19. Structural details of cluster anion **24a**.[84]
Three pentagonal $\{(Mo)Mo_5\}$ fragments and three $\{Mo_2\}$ linkers, which form the $\{Mo_9O_9\}$ metal ring encapsulating the $[(NH_2)_3C]^+$ cation are given in the polyhedral representation and the other (similar) parts of the cluster are in the atomic representation.

cluster capsules (the diameter of the inner cavity is ~16 Å) of the $\{Mo_{72}^{VI}Fe_{30}^{III}\}$ type as hosts and reduced Keggin ions $[H_xPMo_{12}O_{40}]^{3-}$ ($x = 1, 2$; the diameter of the Keggin anion is ~14 Å)[79] as guests. The reduced Keggin ion tightly fits in the cluster cavity, the shortest $O_{guest}\cdots O_{host}$ distances being ~2.6 Å, which is typical of hydrogen bonding. Each of these cluster–cluster composites is linked to four neighbouring ones by Fe–O–Fe fragments, giving rise to a layered structure. The cluster capsule contains twelve pentagonal fragments of the $\{(Mo)Mo_5\}$ type connected by thirty $\{Fe(H_2O)_2\}^{3+}$ linkers. The acetate ligands in them are disordered and are arranged within a sphere, mainly functioning as bidentate bridging ligands between the Mo and Fe atoms.

The binding in cluster–cluster composites is based on the well studied process called inorganic condensation in which the guest molecule acts as the template in the formation of the host (capsule). It is worth noting that composite **23a** can also be prepared by adding a salt of the usual Keggin anion $[PMo_{12}O_{40}]^{3-}$ to the reaction mixture described above devoid of phosphate. The method for the synthesis of composite **23a** is a 'cascade' procedure, which gives the Keggin ion at an initial stage. However, in the presence of greater amounts of phosphate, the reaction follows a different route and composite **23a** cannot be prepared. One more important point is worth mentioning, namely, only iron(II) chloride $FeCl_2\cdot 4H_2O$ is appropriate as the starting reagent, because the use of $FeCl_3\cdot 6H_2O$ results in an amorphous precipitate of a variable composition and structure.

The physicochemical investigations of the structure of **23** (see Ref. 77) not only proved the presence of separate, not bonded by covalent bonds parts (the capsule and the guest) in each spherical unit of cluster **23a** but also revealed interesting topological, spectroscopic, electronic and magnetic properties. For example, nanocapsules of the $\{Mo_{72}^{VI}Fe_{30}^{III}\}$ type form a system of magnetic dots (each of them is the strongest known molecular paramagnet with the spin $S = 150/2$ at room temperature) and, simultaneously, they encapsulate the reduced Keggin ions (quantum dots) as guests. This system can be considered as a potential electron reservoir. It should be emphasised that the free Keggin ion can be reduced in several stages, its charge remaining constant due to the concomitant protonation.[80]

Evidently, knowledge of the chemistry of nanocapsules with a variable size [66, 68] which can be linked together to form polymeric structures [76, 79] is exceptionally important for the synthesis of new polymeric materials with unique properties. In addition, the possibility of introducing guest molecules (a cluster in a cluster) opens up prospects for target-directed variation of the properties of such materials by varying the properties of guests.

VIII. Polyoxomolybdate clusters as nanoreceptors

As has been noted in Section VI, variation of the nature of linkers allows one to change the overall dimensions of spherical objects constructed as {(pentagonal fragment)$_{12}$(linker)$_{30}$} and the dimensions of 20 corresponding pores (Mo_nO_n metal rings); the same structural principle is met for spherical viruses.[81] If the linker is represented by the binuclear $\{Mo_2^V\}$ fragment, the pores on the surface of such spherical system are formed by the $\{Mo_9O_9\}$ rings with a diameter of 0.6–0.8 nm.[62] In the case of mononuclear linkers such as M^{n+} where $M = Fe^{3+}$ (see Ref. 68), MoO^{3+} (see Ref. 66) or VO^{2+}/MoO^{3+} (see Ref. 72), smaller rings are formed, namely, $\{Mo_6O_6\}$, whose size is just appropriate for 'trapping' potassium cations.[82] Note that every one of these 20 pores (rings) has, in principle, the properties of a receptor comparable with those of crown ethers, which are classical objects of supramolecular chemistry.[83] It has been shown [84] that spherical clusters like $\{Mo_{132}\}$ with different types of ligands stabilising the $\{Mo_2^VO_4\}^{2+} \equiv \{Mo_2^V\}$ groups have pores the sizes (Fig. 18) of which allow encapsulation of rather big complementary substrates present in solution, for example, guanidinium cations. This is especially important, as guanidine, acting as a ligand [85, 86]

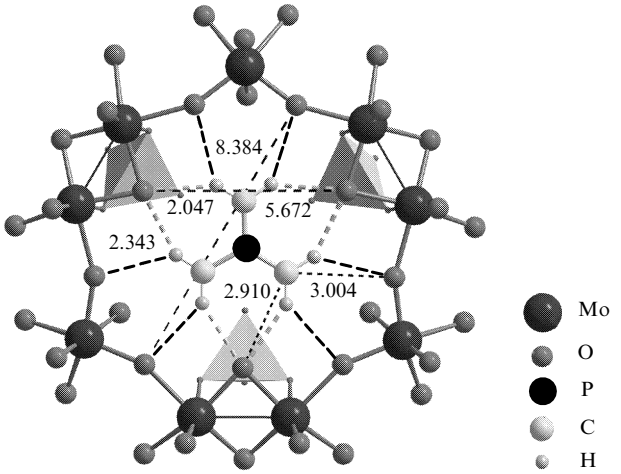


Figure 20. Interatomic distances in the $\{Mo_9O_9\}$metal rings reflecting the interaction between receptors and substrates.[84]

or a receptor of anions [87] and functioning as a sterically flexible molecule, plays a noticeable role in coordination chemistry, supramolecular chemistry and solid state chemistry and is often used in the chemical design for the formation of cross-linked structures.[88] For example, the $[\{(Mo)Mo_5O_{21}(H_2O)_6\}_{12}\{Mo_2^VO_4.(H_2PO_2)\}_{30}]^{42-}$ (**14a**) cluster reacts with guanidinium sulfate to give the compound $[\{[(NH_2)_3C]^+\}_{20} \subset \{(Mo)Mo_5O_{21}(H_2O)_6\}_{12}.\{Mo_2O_4(SO_4)\}_{10}\{Mo_2O_4(H_2PO_2)\}_{20}]^{32-}$ (**24a**) as a crystalline salt (Fig. 19).

In the structure $\{[(NH_2)_3C]^+\}_{32}\{[(NH_2)_3C]^+\}_{20} \subset \{(Mo)Mo_5.O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(SO_4)\}_{10}\{Mo_2O_4(H_2PO_2)\}_{20}]^{32-}\cdot 200\,H_2O$ (**24**), the guanidinium cations fit exactly into the pores, *i.e.*, the $\{Mo_9O_9\}$ rings, owing to their size and symmetry, and are bound by hydrogen bonds formed between the bridging oxygen atoms of the binuclear $\{Mo_2^V\}$ groups of the metal rings and the NH_2 groups of the cations. The same type of binding of guanidinium cations has been observed for monotopic receptors [89] (Fig. 20).

It should be emphasised that in this case, highly important is the possibility of 'plugging' 20 pores of the giant spherical cluster where the pore sizes are large enough for relatively small substrates to enter the central cavity. This provides the possibility of complete removal of these substrates from a solution — which would be a phenomenon comparable with substrate recognition by nanosponges.[89] The plugging of pores substantially decreases the negative charge of the cluster, stabilises the cluster and affects the structure of the unique water cluster $\{H_2O\}_n$ (see Ref. 90), which is disordered in the case of polyoxometallate clusters with open pores.[91] This process can formally be compared with the process in which a cell converts the extracellular response.[92] In the absence of encapsulated cations, the structure of the water cluster is determined by interactions with water of crystallisation through open pores.[84] In the case of anion **24a**, the central cavity contains only highly symmetrical $\{H_2O\}_n$ polyhedra — clusters with endohedral hierarchy — an $\{H_2O\}_{20}$ dodecahedron is embedded into an $\{H_2O\}_{60}$ rhomboicosidodecahedron, which is in turn embedded into another $\{H_2O\}_{60}$ rhomboicosidodecahedron.

Thus, various spherical clusters of the keplerate type possess a large number of receptor centres and can act as receptors for both cations and neutral substrates. The variation of linkers (*i.e.*, mono- and binuclear metal centres) makes it possible to change the pore size in metal rings and, hence, such clusters can act as effective and specific nanosponges with respect to complementary substrates. In addition, the reactivity of such nanosponges should differ from the reactivity of monotopic receptors and should change with a change in the electronic properties of the cluster shell.[93] This can be compared with the situation where the substrates have been applied onto 'classical' surfaces, for example,

onto industrial metal oxide catalysts,[94] and the reactivity of these substrates can also change upon the variation of the surface properties.[95]

* * *

The data presented in this review demonstrate the scope and prospects of the inorganic synthesis of compounds of a new type — large polyoxometallate clusters of various structures. These objects, the properties of which are being currently studied, are of interest not only from the standpoint of fundamental chemistry but, apparently, can also find application in processes of chemical industry as catalysts and bioactive substances. However, the most important point is that in relation to these compounds, one can follow the development of a new field of chemistry — the chemistry of molecular materials, which are materials of the future.

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