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Authors' Review

Polyoxomolybdates and Polyoxomolybdovanadates – from Structure to Functions: Recent Results*

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Abstract. The authors' review compiles the literature in the field of polyoxomolybdates, POMo, and polyoxomolybdovanadates, POMoV, over the past two decades. The main achievements in the field of synthesis, crystal and molecular structure determinations and applications are presented. The first section describes polyoxomolybdates; their structure starting with a smaller number of building units to the formation of new structural shapes of polyoxomolybdate clusters of supramolecular arhitecture. Polyoxomolybdates include the compounds with various organic ligands, functionalized polyoxomolybdates and a number of organo-inorganic clusters. Recent synthetic methods such as functionalization and hydrothermal/solvothermal synthesis with a possibility to control the size and shape of the resulting structure are reviewed. The design and synthesis of inorganic-organic hybrid compounds in which POMo anions are combined with organic molecular cations appears as the most successful approach for preparing novel types of molecular based materials with functional properties. The second section covers the polyoxomolybdovanadate compounds from structure to synthesis. Interesting compounds with the molybdenum-rich region or vanadium rich-region, mixed vanadium-molybdenum polyoxoanions with various oxidation states of the metal atoms and the organic-inorganic hybrid materials are described. The last section reviews the application of the before mentioned compounds. Due to the functionalization of the complexes potential utility in biology and medicine, catalysis and material science is significantly increased. Finally, the importance of large polyoxometalate clusters as target nanosized molecular materials, which present a challenge for the future complex chemistry, is discussed.

Keywords: polyoxomolybdates, polyoxomolybdovanadates, synthesis, crystal and molecular structure, application

INTRODUCTION

Polyoxometalates (POMs) represent a large class of metal-oxygen cluster anions which exhibit compositional diversity, structural versatility and remarkable physicochemical properties.[1] Though the first polyoxometalates were described by Berzelius as early as 1826, the knowledge of their complex structure progressed very slowly.[2] A number of scientists were involved to solve the structure and composition of those compounds, but only the development of modern, sophisticated and high-resolution instrumental techniques helped to understand fundamental chemistry and structure of POMs.[3] Due to this knowledge the polyoxometalate chemistry has moved rapidly forward.[4,5] In recent years a number of new highly complex compounds have been prepared starting from simple building blocks to very large complex molecular systems by linking a huge variety of basic and well defined fragments.[6,7] The synthesis of the wheel- and sphere-shaped giant molybdenum oxide based clusters have rised high expectation in nanotehnology and material science.

The development of a new class of functionalized polyoxometalates in which an organic ligand replaces a terminal oxo ligand within the parent structure, have been extensinvely studied last two decades.[5,8,9] Furthermore, POMs based hybrid materials namely structures of molybdenum and vanadium oxides contribute to the specific properties.[10,11] The understanding of structure-synthesis relationship of polyoxomolybdates, hybrid structures of polyoxomolybdovanadates and functionalized polyoxomolybdates followed to assess the desired

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* Dedicated to Professor Emeritus Drago Grdenić, Fellow of the Croatian Academy of Sciences and Arts, on the occasion of his 90th birthday.

** Author to whom correspondence should be addressed. (E-mail: marina@chem.pmf.hr) molecular structure and morphology in order to extend a variety of important applications such as catalysis, analytical and clinical chemistry, photochemistry, solid state devices, biochemistry and biomedical application.[5,12]

The review covers the synthesis, structure and applications of polyoxomolybdates and molybdovanadates in the last decade. The achievements of the new synthetic methods and potential for the formation of nanoscopic molecules in POMs cluster chemistry and their structural diversity is emphasized.

POLYOXOMOLYBDATES

Characteristic Structures

POMs can be described in terms of assemblages of metal-centered MO_n polyhedra that are linked by shared corners, edges and rarely faces. According to M. T. Pope the structures of polyoxoanions are the result both of a favourable combination of ionic radii and charge and of accessibility of empty d orbitals for metal-oxygen π-bonding. Their structures are governed by two general principles:[3]

- Each metal atom occupies an MO_n coordination polyhedron (most commonly an octahedron or square pyramid) in which the metal atoms are displaced as a result of M–O π-bonding towards those polyhedral vertices that form the surface of the structure. Structures with MO_6 octahedra that contain three or more free vertices are, in general, not observed.
- The second principle known as Lipscomb restriction, has been rationalized in terms of the strong *trans* influence of the terminal M–O bonds, which facilitates dissociation of neutral (MO_3) from the cluster.[13] This restriction is not absolute, particularly in aqueous solutions.

In general, the polyoxoanion structures are packing of octahedra with common edges, but observed are only some of the possible packing combinations. According to D. L. Kepert such packing is a result of the repulsion forces between $M^{n+}\cdots M^{n+}$ ions.[14] Following this Kepert ideas the empirical «*rules of compactness*» have been developed. According to these rules in the packing of the octahedra with common edges the fundamental structural motif for POM is the pair of edge-sharing octahedra. Applying such a principle the shape of poly-anions can be derived by adding additional octahedra in the edge–sharing fashion to this structural motif. Thus the third octahedra may be added in several ways to generate possible trinuclear core structure. Further expansion of the aggregates by linking forth or more octahedra may be accomplished by the *rule of compactness*. Under specific conditions it is possible to build step-wise from simple packing blocks of the octahedra larger molecular systems of a size even comparable to that of proteins.[6] In the majority of structures molybdenum atoms are octahedrally coordinated by six oxygen atoms, although known are coordination polyhedra with four (tetrahedral) and five (square pyramidal and trigonal bipyramidal) oxygen atoms. $(MoO_4)^{2-}$ is tetrahedral, $(Mo_2O_7)^{2-}$ two tetrahedra sharing common corner, trimolybdates are polymeric with infinite chains of octahedra with common edges and corners (possible are additional tetrahedra or square pyramids).

Di-, Tri-, Tetra- and Pentamolybdates

A number of molybdenum oxalates of the general formula $R_2[Mo_2O_5(C_2O_4)_2(H_2O_2)_2]$ were prepared and analyzed.[15–17] The complexes are built up of the dimeric anions containing Mo_2O_5 core. Molybdenum atoms exhibit distorted octahedral coordination. It should be pointed out that the angles at the bridging oxygen atom in dinuclear anion differ significantly depending upon the size of the cation, crystal structure packing conditions and by additional hydrogen bonds. The cation of larger ionic radii may induce distortion of the dimeric anion causing bending of the Mo–O–Mo bridge,[18] and it has also the effect on the polymeric structure (Figure 1).[17]

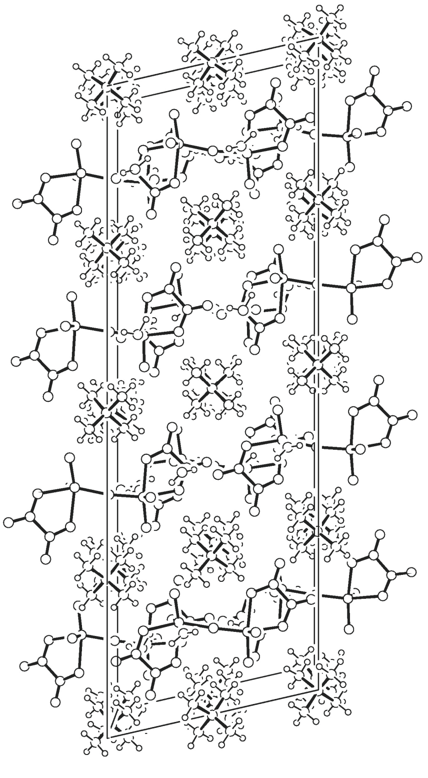


Figure 1. Polymeric structure of $[Mo_2O_5(C_2O_4)_2(H_2O)_2]^{2-}$ anions (adapted from Ref. 16).

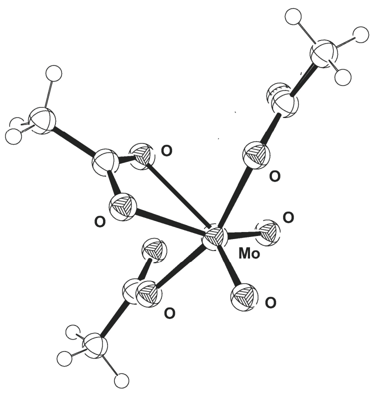


Figure 2. The structure of $[Mo_2O_4(OCOCH_3)_6]^{2-}$ anion (adapted from Ref. 19).

Those complexes of Mo^{VI} are of interest owing to their photochromic properties. According to ESR measurements the exposure of the complex to UV radiation changes oxidation number of Mo from +6 to +5. The first structuraly characterized example of dinuclear molybdenum(VI) acetato complex was $Na_2[Mo_2O_4(OCOCH_3)_6]\cdot NaOCOCH_3\cdot CH_3COOH$.[19] Dinuclear complex anion, $[Mo_2O_4(OCOCH_3)_6]^{2-}$, is a centrosymmetrical interconnected by sodium cations and centrosymmetrical pairs of acetate-acetic acid. Two acetate ligands are monodendately bonded to each molybdenum atom while the third one together with its centrosymmetrical pair acts as a bridge with Mo–O distances of 2.169(2) and 2.222(2) Å. They are the longest Mo–O bonds due to the *trans* influence of the terminal oxo-oxygen atoms (Figure 2).[19]

A very interesting Mo complex prepared solvothermally $(C_4H_{12}N_2)_2[(Mo^{V}_2O_4)(Mo^{VI}O_4)(C_2O_4)_2]\cdot 2H_2O$ reveals that the compound consists of novel molybdenum–oxide helical chains with oxalate groups coordinated directly to the Mo(1) and Mo(2) sites (see Figure 3). The 1D helical chain is composed of the dinuclear units of edge-sharing (MO_6) octahedron linked by (MO_4) tetrahedron through corner-sharing. Charge compesation is achieved by the protonated piperazine of the skeleton.[20]

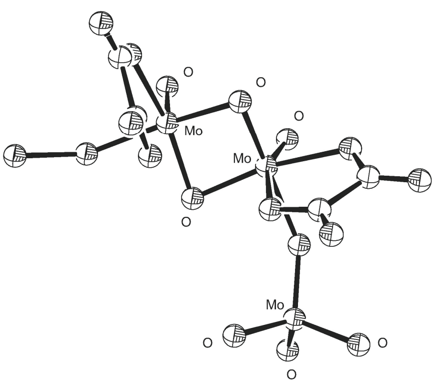


Figure 3. Different coordinations of Mo atoms in $[(Mo^{V}_2O_4)(Mo^{VI}O_4)(C_2O_4)_2]^{2-}$ anion (adapted from Ref. 20).

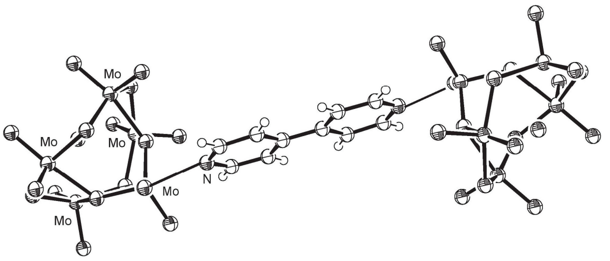


Figure 4. Structure of polyanion $[(Mo_5O_{17})_2(4,4'\text{-bipy})]^{8-}$ (adapted from Ref. 25).

By hydrothermal approach the alkali trimolybdates were prepared with a distorted variation of $(Mo_3O_{10})^{2-}$ chains as a key structural motif found previously only in $(C_2H_{10}N_2)[Mo_3O_{10}]$ complex.[21] The arrangement of the Mo–O polyhedra within the chain of alkali trimolybdates and the resulting structure strongly depends upon the size of alkali cation (Rb, K, Cs).[22]

The tetranuclear polyoxomolybdate(V) anion $[Mo_4O_8(OH)_2(H_2O)_2(C_2O_4)_2]^{2-}$ is built up of four edge–sharing distorted octahedra, separated in two pairs corresponding to Mo^{V}–Mo^{V} dimers with localized metal–metal bonds. Two μ_2-bridging ligands stabilize the oxomolybdate core. Valence bond calculations have shown that two bridging oxygen atoms are hydroxo ligands and two terminal oxygen atoms belong to water molecules.[23] Another tetranuclear polyoxomolybdate complex $[(CH_3)_4N]_2[Mo_4O_{10}(OCH_3)_4Cl_2]$ with a centrosymetric anion has four edge-sharing octahedra, two MO_6 and two MO_5Cl. As a result of displacement of metal ions towards the polyanion surface, all four octahedra are distorted. All bond lengths and angles are comparable with those previously observed tetranuclear complexes.[24]

A dimeric pentamolybdate prepared hydrothermaly $[4,4'\text{-}H_2bipy]_3[4,4'\text{-}Hbipy]_2[(Mo_5O_{17})_2(4,4'\text{-bipy})]$ is an example of polyanion $[(Mo_5O_{17})_2(4,4'\text{-bipy})]^{8-}$ with two identical pentamolybdenum ions and one 4,4'-bipyridine molecule (see Figure 4).

The anion is composed of four MO_6 octahedra and one MO_4N unit with trigonal bipyramidal coordination geometry. The five protonated 4,4'-bipyridine molecules act as counter ion to the polyanion thus giving charge-compensating and space-filling metal oxide/organic material structure.[25]

Hexa- and Heptamolybdates

Hexamolybdate anion is well known in the structural chemistry of polyoxomolybdates. In this structure oxygen atoms form close packed structures (three layers) in a cubic close packing feature with Mo–atoms occupying octahedral holes, imitating a fragment of the sodium chloride structure. The crystal structure of bis(tetramethylammonium) hexamolybdate hydrate is an example of Lindquist type hexamolybdate anion $(Mo_6O_{19})^{2-}$. Each Mo atom is coordinated by six O atoms (one terminal, one central and four bridging) in a distorted octahedral arrangement due to the displacement of Mo atoms toward the terminal O atoms. The six MO_6 octahedra share common vertex at the central O atom and also each octahedron shares four edges with adjacent octahedra.[21] Recently most of the hexamolybdates[26] and octamolybdates were functionalized *i.e.* replacing of one or several oxo ligands by other ligands. By introducing suitable terminal ligands the properties of polyoxomolybdates can be tuned and their application expanded in different fields. A series of Lindquist-type aryldiazemido polyoxomolybdates of the type $(Bu_4N)_3[Mo_6O_{18}(N_2Ar)]$ have been investigated.[27] The aryldiazemido ligands exhibit features characteristic of the singly bent coordination mode with short Mo–N and N–N bonds indicative of multiple–bond character. The substituents on the aromatic rings influence the physical and chemical properties of the hexamolybdate which have been examined in details by ^{95}Mo and ^{17}O NMR spectroscopy, UV/VIS spectroscopy.[27] A large class of organoimido derivatives of $(Mo_6O_{19})^{2-}$ comprising both singly and multiply functionalized hexamolybdate has been prepared.[8] In the case of singly functionalized imidohexamolybdates by three ligands (butyl, cyclohexyl, 2,6-diisopropylphenyl), the ligand occupies a terminal site of hexamolybdate cage. The short Mo–N bond lengths (1.711–1.739 Å) are typical of organoimido ligands bound to an octahedral d^0 metal centre and are consistent with a substantial degree of M≡N triple bond character. Multiple functionalization has been achieved with 2,6-(diisopropyl)phenilimido ligand (NAr). The organoimido ligands, starting from 2 to 5, occupy terminal position and the metrical parameters associated with the [Mo≡NAr] units are unexceptional. Within each of the multiply supstituent species the central oxygen is again displaced away from the [O≡Mo] site toward the *trans*-[Mo≡NAr] site. Mo–O_b (O_b – bridging oxygen atom) bond lengths are generally longer at [Mo≡NAr] sites than at [O≡Mo] sites. Functionalization induces a range of perturbations. Each of the organoimido ligands examined furnishes more electron density to the hexamolybdate cage than does an oxo ligand rendering the $[Mo_6O_{18}(NR)]^{2-}$ complexes more difficult to reduce than the $(Mo_6O_{19})^{2-}$ parent. One of the structural consequences of this donation is a consistent lengthening of the Mo–O bond length at the imido bearing sites as compared to those at the terminal oxo sites. Multinuclear NMR results suggest that the electron density accumulates preferentially at the terminal oxo ligands rather than within the (Mo_6O_{13}) core. In addition, phenylimido derivatives of $(Mo_6O_{19})^{2-}$ were prepared and characterized.[9] Mono- and di- phenylimido complexes $[Mo_6O_{18}(NPh)]^{2-}$ (**1**) and $[Mo_6O_{17}(NPh)_2]^{2-}$ (**2**) were found in the solution and recrystalized samples. The unit cell of both **1** and **2** complexes contains four hexamolybdate anions and eight tetrabutylammonium cations. Both samples are a mixture of at least two different anions. The substitution introduces a distortion of the hexanuclear core of molybdenum. Some Mo–O bonds are significantlly shorter than the average of other Mo–O distances which could indicate the *trans* influence of the phenylimido ligand. The NMR results, Raman and electrochemistry results confirmed the above mentioned species and the characteristics of the individual components in solution.

The $[Mo_7O_{24}]^{6-}$ anions have been confirmed as the predominant species in aqueous solution at pH = 3 to 5.5. The heptamolybdate anion has been characterized by numerous solution studies and by the structures of $[NH_4]_6[Mo_7O_{24}]\cdot 4H_2O$,[28] $K_6[Mo_7O_{24}]\cdot 4H_2O$,[29] for example, all of which may be crystallized from aqueous solution. Raman spectroscopy and X-ray investigation confirm that the structure of the anion is unchanged in solution. A large number of POM-based organic and inorganic hybrid materials have been prepared. In the subclass of hybrid materials based on isopolymolybdate cluster units, however, the polyanions are limited to $\{Mo_3O_{10}\}$, $\{Mo_4O_{18}\}$, $\{Mo_6O_{19}\}$, and $\{Mo_8O_{26}\}$, clusters. Hybrid solid materials based on heptamolybdate are rare and therefore, it remains a great challenge to prepare new heptamolybdate-based organic and inorganic hybrid materials. One of the interesting examples is a new supramolecular compound, $(Hapy)_4[Co(H_2O)_5\text{-}Mo_7O_{24}]\cdot 9H_2O$,[30] isolated by hydrothermal synthesis.

Octamolybdates and Related Compounds

The main characteristic of the octamolybdates is their diversity. The octamolybdate anions are built up from eigth condensed octahedra with 16 terminal positions. The bond lengths depend again upon the nature of the bond as well as upon the position within the structure (*e.g. cis* or *trans* with respect to the Mo=O bond). The α-, β- and γ- structures are based on the cubic close packed structure with Mo atoms occupying the octahedral sites (Figure 5).

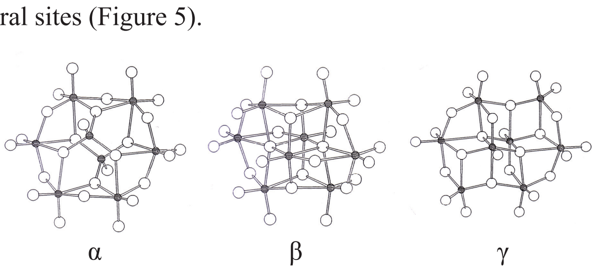


Figure 5. Structures of α-, β-, γ-polyoxooctamolybdates.

The recent expansion of coordination chemistry of the polyoxooctamolybdates displays interesting metal-ligand reaction chemistry. Most of such octamolybdates have a general formula $[\mathrm{Mo_8O_{26}(L)_2}]^{(2n-4)}$ where *n* is a formal charge of L. Two sites of the $\mathrm{Mo_8O_{28}}$ core are usually occupied by the ligand L. A number of octamolybdates functionalized with organic ligand have shown antitumor activity. This is the case with γ-octamolybdates with aminoacids (DL-alanine) and peptides: $\mathrm{Na_4[Mo_8O_{26}(alaO)_2]\cdot 18H_2O}$ (**1**) (Figure 6), $\mathrm{Na_4[Mo_8O_{26}(glyglyO)_2]\cdot 15H_2O}$ (**2**) and $\mathrm{Na_4[Mo_8O_{26}(glyglyO)_2]\cdot 12H_2O}$ (**3**).[31] All three crystal structures are composed of γ-octamolybdate complex anion, sodium cations and water molecules. The anions consist of eight condensed edge-sharing $\mathrm{MO_6}$ octahedra with 16 terminal position and 14 of them occupied by oxo-oxygen and two by carboxylato-oxygen anions as shown in Figure 6. The bond lengths in all three octamolybdate anions are mutually in very good agreement. Main structural difference in those three structures is observed in their packing diagrams. In $\mathrm{Na_4[Mo_8O_{26}(alaO)_2]\cdot 18H_2O}$, solvated water molecules makes these crystals relatively unstable. The glycylglycine ligands in structures **2** and **3** have different packing mode. In the same group of functionalized octamolybdate complexes displaying biological activity the complex of $\mathrm{Na_4[Mo_8O_{26}(proO)_2]\cdot 22H_2O}$ is included.[32] The DL-proline ligands are attached to molybdenum atoms *via* monodendate carboxylate-oxygen atoms. An intramolecular hydrogen bond is formed between the proline amino hydrogen, while the free carboxyl oxygen atom of the proline ligand is contacting oxygens of a sodium-water chain.

The structures of $\mathrm{[NH_3Pr]_2[Mo_8O_{22}(OH)_4(OC_6H_4CH{=}NPr\text{-}2)_2]\cdot 6MeOH}$ (**1**) and $\mathrm{[Hmorph]_4[Mo_8O_{24}(OH)_2(MetO)_2]\cdot 4H_2O}$ (**2**) consist of eight centrosymmetrically edge-sharing octahedra.[33] Similarly to the previously described structures, out of 16 terminal positions 14 are occupied by oxo-oxygen atoms and two by the salycilideneiminato (**1**) or methioninato oxygen (**2**) atoms. Of the remaining 12 oxygen atoms six are double-bridging two Mo atoms, four O atoms are triple-bridging three Mo atoms, while two O atoms are four bridging four Mo atoms. The consequence are varying Mo–O distances from 1.77 to 2.44 Å. In both cases salycilideneiminato and methioninato–oxygens are stronger donors so that Mo–O but not Mo–N or Mo–S bonds are formed.

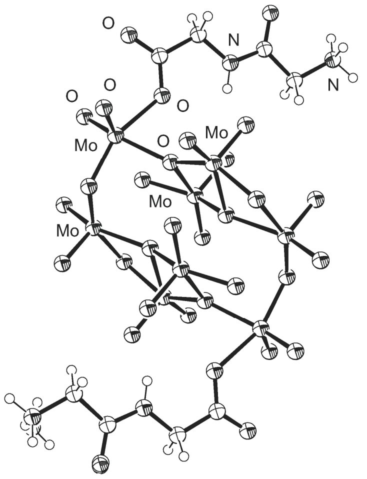


Figure 6. Structure of anion in $\mathrm{Na_4[Mo_8O_{26}(glyglyO)_2]\cdot 15H_2O}$ (adapted from Ref. 31).

A new polyoxomolybdate supramolecular architecture was obtained from $\gamma\text{-}(\mathrm{Mo_8O_{26}})^{4-}$ anions with nicotinato ligands $\mathrm{(Himi)_4[Mo_8O_{26}(nic\text{–}O)_2]}$.[34] (imi = imidazole, nic-OH = nicotinic acid). The nicotinic acid ligand coordinates the octamolybdate unit by its carboxylic oxygen atom. The oxygen atoms within anion clusters can be divided in four sets according to their bonding feature as in the above described structure. Each $[\mathrm{Mo_8O_{26}(nic\text{–}O)_2}]^{4-}$ cluster is connected to four adjacent clusters by two kinds of hydrogen bonds: N–H···O and C–H···O. The hydrogen bonding contacts result in an extended 2D network in (101) plane, while the hydrogen bonding between imidazole cations and anion clusters assembles in the 3D supramolecular structure. Polymeric octamolybdate clusters with organic cations participating in bridging interactions were found in the morpholinium β-octamolybdate tetrahydrate.[35] A polymeric oxomolybdate(VI) $\mathrm{(Me\text{-}NC_5H_5)_{4n}(Mo_8O_{26})_n}$ consists of *N*-methylpyridinium cations and infinite anionic molybdenum oxide chains built of the eight-octahedra units and connected through pairs of Mo–O–Mo bridges into extended one dimensional arrays (Figure 7).[36]

Similar chain structure is found in $\mathrm{(C_4H_{14}N_2)_2(Mo_8O_{26})\cdot 2H_2O}$,[37] where eight $\mathrm{(MoO_6)}$ octahedra share both edges and vertices, forming the $\mathrm{(Mo_8O_{26})}_n^{2n-}$ chains. $\mathrm{(C_4H_{14}N_2)^{2+}}$ cations and occluded water molecules reside between chains and participate in an extensive hydrogen-bonding network thus stabilizing the structure.

A number of organic-inorganic hybrid materials using POMs as building blocks have been recently successfully prepared. The hybrid compound $\mathrm{[Co(bpy)_3]_2(Mo_6O_{19})[\beta\text{-}(H_2Mo_8O_{26})]\cdot 4H_2O}$ consists of racemic

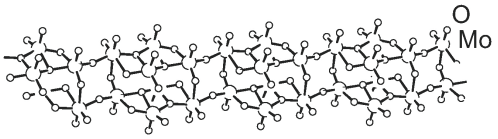


Figure 7. Infinite chains of $[\mathrm{Mo_8O_{26}}]_n^{4n-}$ anion (adapted from Ref. 36).

complexes $(-/+)[Co(bpy)_3]$ and both $(Mo_6O_{19})^{2-}$ and β-$(Mo_8O_{26})^{4-}$ anions.[38] The most remarkable structural distinction of β-$(Mo_8O_{26})^{4-}$ from $(Mo_6O_{19})^{2-}$ is that the former contains MO_6 octahedron with two terminal O atoms, while the latter involves MO_6 octahedron with only one terminal O atom. Furthermore, $[Co(bpy)_3]^{2+}$ complex parts are in racemic enantiomorphous architecture. Each Co^{2+} site is surrounded by six nitrogen atoms from three 2,2'-bipyridine molecules and forms a distorted CoN_6 octahedron. In the solid state these three subunits are presented in the respectively independent form, though there is O···H–O hydrogen bonding between β-$(Mo_8O_{26})^{4-}$ anions mediated by free water molecules.

Another polyoxomolybdate organic hybrid is a compound $(Bu_4N)_8(Mo_6O_{19})_2[\alpha\text{-}Mo_8O_{26}]$ in which $(Mo_6O_{19})^{2-}$ coexists with α-$(Mo_8O_{26})^{4-}$ anions alternatively arranged in crystal architecture.[39] The crystal structure is presented as layers of both anions, alternatively arranged in (011) planes. The counterions $(Bu_4N)^+$ are regularly distributed in the interspace formed by polyanions and show three kinds of weak interactions with inorganic layers. Two new organic-inorganic hybrid compounds based on polyoxomolybdates differing in their solvent content were explored; commensurate $(H_2DABCO)_2[Mo_8O_{26}]\cdot 4H_2O$ (**1**) and incommensurate $(H_2DABCO)_2[Mo_8O_{26}]\cdot 4.66H_2O$ (**2**) (1,4-diazabicyclo[2.2.2]octane = DABCO).[40] The compound **1** is composed of self-assembly of $(Mo_8O_{26})^{4-}$ anionic chains, $(H_2DABCO)^{2+}$ cations and water molecules. The anionic chain is built up from γ-$(Mo_8O_{28})^{8-}$ octamolybdate cluster. The structure of **2** resembles that of **1** except by its water molecule and $(H_2DABCO)^{2+}$ content and ordering, which generate the incommesurability. The complex hydrogen-bond network is observed not only between the cations and the water molecules or between the anionic chains and the water molecule, but also between some of the cations and the polyoxometalate chains. Though this kind of hydrogen bond is a prerequisite for their photochromic properties none of the compounds is photochromic. Under hydrothermal conditions a variation of the structures of β-octamolybdate, (Mo_8O_{26}), clusters were obtained. A variation of the structures is mainly due to the differences in the connectivity between the (Mo_8O_{26}) clusters.[41] The structure of $[NH_3(CH_2)NH_3]_2(Mo_8O_{26})\cdot H_2O$ (**1**) consists of octahedrally coordinated Mo atoms connected through their edges forming $(Mo_4O_{13})^{2-}$ units. Two $(Mo_4O_{13})^{2-}$ subunits give rise to β-octamolybdate clusters forming infinite anionic one–dimensional chains. The structure of $[NH_3(CH_2)NH_2(CH_2)_2NH_3]_2(Mo_9O_{30})$ (**2**) is built up of similar β-octamolybdate cluster units. The MO_6 octahedra occupy a special position sitting on the inversion center. The one-dimensional chain of the formula (Mo_9O_{30}) have helicity with both the right-handed and the left-handed units present in adjacent chains. The structure of $[NH_3(CH_2)NH_2(CH_2)_2NH_3]_2(Mo_{10}O_{33})$ (**3**) is made up from the connectivity between the (Mo_8O_{26}) cluster units and (Mo_8O_7) units. The resulting $(Mo_{10}O_{33})$ chain has a *zigzag* character. The organic amine molecules occupy the interchain regions. Those compounds provide a novel example of the retention of the geometry of the molecular building blocks in the synthesis of the solid-state materials.

On the example of the nitrosyl derivative of decamolybdate $[Mo_{10}O_{25}(OMe)_6(NO)]^-$ an important role of delocalization of «blue electrons» is presented.[42] Several isomers differing by position of methyl groups have shown that the electron delocalization patterns can be modulated. Two Mo–O–Mo interactions are responsible for the electron delocalization, namely within the same equatorial plane and between two planes. The study also demonstrated the transition from the delocalization to the magnetic exchange mechanism of spin pairing in reduced polyoxomolybdates. This transition is a consequence of the chemical bonding perturbation by the protonation of bridging oxygen atoms in Mo–O–Mo fragments. Thus the polyoxomolybdates appears to be a versatile building block for the construction of molecular magnetic materials.

The formation of new structural types of polyoxomolybdate cluster has been recently demonstrated. Away from the symmetrical spherical structures (Lindquist, Keggin, Dawson) a strategy to define a new type of nonspherical, low–symmetry and lower–nuclearity clusters as building blocks have been presented.[43] Such clusters restrained by «shrink–wrapping» display an unprecedented topology, low symmetry and high negative charge: $(C_6H_{13}N_4)_{10}(H_2Mo_{16}O_{52})\cdot 34H_2O$ (**1**) and $(C_6H_{13}N_4)_6[Fe_2(H_2O)_8H_2Mo_{16}O_{52}]\cdot 8H_2O$ (**2**).

The cluster **1** consists of negatively charged framework of $[H_2Mo_{16}O_{52}]^{10-}$ and displays an unusual flat shape with Mo centers to be $Mo_4^VMo_{12}^{VI}$. The four Mo^V centers comprise two centrosymmetrically related Mo_2^V group which display a short Mo–Mo contact of 2.642(7) Å, characteristic of Mo–Mo single bonds. The «body» of the cluster consists of central unit with twelve Mo atoms and two «wings» each with two molybdenum centers. In the case of **2** two $[Fe_2(H_2O)_4]$ units are each coordinated to the two terminal oxo ligands attached to Mo^{VI} and Mo^V. This compound also indicates weak but significant intramolecular antiferromagnetic exchange interactions between Fe^{II} centers. Another mixed–valence polyoxomolybdate $[H_2Mo_{16}O_{52}]^{10-}$ using protonated hexamethylenetetramine $(HMTAH)^+$ as counter ion exhibits significant nucleophilicity and can trap electrophiles such as divalent transition metal ions resulting in a family of isostructural compounds.[44] The highly reactive $\{Mo_{16}\}$ system undergoes to rearrange-

Table 1. Giant polyoxomolybdate clusters formulated according to metal-based building blocks $\{(Mo)Mo_5\}$[45]

Building core	Ligand	Synthesis	Reference
Mo_2O_4	acetate oxalate	solution, solvothermal	19 20
Mo_2O_5	oxalate	solution	15–17
Mo_4O_8	oxalate	solution	23
Mo_4O_{10}	2-hydroxy-nicotinate	solution	24
Mo_5O_{17}	4,4'-bipyridine	hydrothermal	25
Mo_6O_{12}	methoxy acetylacetonate	solution	22
Mo_6O_{18}	aryldiazemide	solution/ functionalization	26
Mo_6O_{19}	organoimido	solution/ functionalization	8, 9
Mo_8O_{22}	salycilideneiminate	solution/ functionalization	32
Mo_8O_{24}	methioninate	solution	32
$Mo_{10}O_{25}$	methoxy	solution	42
Mo_8O_{26}	alaninate glycilglycinate	solution/ functionalization	30
	prolinate		31
	nicotinate	hydrothermal	33

ment and decomposition reaction. The crystal structure of $[H_2Mo_{16}O_{52}]^{10-}$ anion is centrosymmetric with four formal Mo^V centers organized as two inversion symmetry related $\{Mo_2^V\}$ pairs with Mo–Mo short distances of 2.612(2) Å a motif typical for mixed-valence polyoxomolybdate structures. Sixteen MO_6 octahedra decompose the cluster into a central $\{Mo_{12}\}$ building block and two $\{Mo_2\}$ groups. Eight Mo positions of the $\{Mo_{12}\}$ building block are arranged along the lines to form two inversion-related backbones. The other four Mo centers at the ends of the two backbones unite the two backbones through bridging ligands. The inherent reactivity of highly charged cluster anions is revealed by gradual decomposition to smaller $\{Mo_7\}$ units in the solution and in the presence of divalent transition metal cations produce clusters of different arrangements. $\{Mo_{16}M_2\}$ adducts demonstrate the efficiency of polyoxomolybdates in mediating magnetic superexchange. Described polyoxometalates are summerized in Tables 1 and 2.

Table 2. Polyoxomolybdates formulated according to building core and ligands

Building block/ anion	Ligand	Synthesis	Reference
$(Mo_7O_{24})^{4-}$	$[Hapy]^{4+}$	hydrothermal	29
$(Mo_8O_{26})^{n-}$	$[Me\text{-}NC_2H_5]_4^+$	hydrothermal	36
$(Mo_8O_{26})_n^{2n-}$ $(Mo_6O_{19})^{2-}$	$(C_4H_{14}N_2)^{2+}$	water solution	37
β-$(Mo_8O_{26})^{4-}$ (racemic cop.)	$[Co(bipy)_3]^{2+}$	hydrothermal	38
$(Mo_6O_{19})^{2-}$ α-$(Mo_8O_{26})^{4-}$	$(Bu_4N)^+$	hydrothermal	39
$(Mo_8O_{26})^{4-}$ γ-$(Mo_8O)^{8-}$	$(H_2DABCO)^{2+}$	hydrothermal	40
$(Mo_8O_{26})^{4-}$ (two $(Mo_4O_{13})^{2-}$ units)	$[NH_3(CH_2)NH_3]^{2+}$	hydrothermal	41
$(H_2Mo_{16}O_{52})^{10-}$ (mixed valence	$(C_6H_{13}N_4)^+$	solution	43
(Mo^V, Mo^{VI}))	$(HMTAH)^+$	solution	44

Giant Polyoxomolybdates

Complex polyoxomolybdate clusters are prepared in a step-wise manner from smaller well-defined fragments. The strategy of self-aggregation and the variety of shapes and functionality of large clusters (Figure 8) are described in excellent papers by A. Müller and collaborators.[45,46]

As an arhetypical example building blocks containing 17 metal atoms $\{Mo_{17}\}$ units can link to form

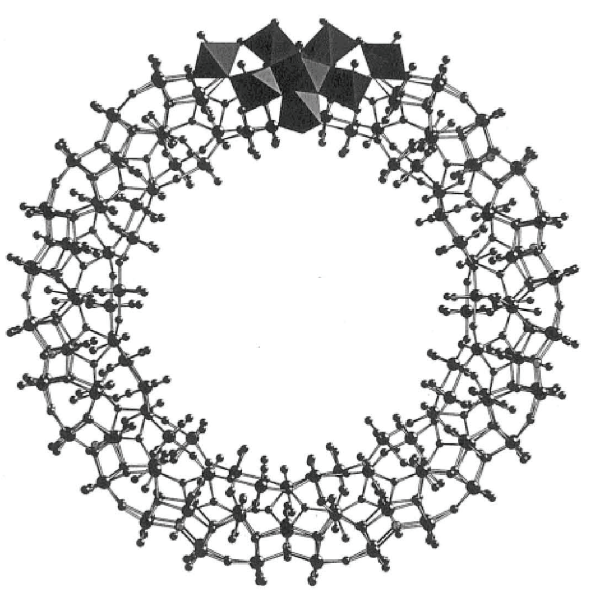


Figure 8. Giant polyoxomolybdates (adapted from the Ref. 45).

Table 3. Polyoxomolybdates: organo-inorganic hybrid materials

Cluster	Formulation based on largest building blocks	Smaller building blocks of the larger groups
$\{Mo_{36}\}$	$\{Mo_{17}\}_2\{Mo_1\}_2$	$\{Mo_{17}\} = \{(Mo)Mo_5\}_2\{Mo\}_5$
$\{Mo_{146}\}$	$\{Mo_8\}_{16}\{Mo_2\}_9$	$\{Mo_8\} = \{(Mo)Mo_5\}\{Mo\}_2$
$\{Mo_{154}\}$	$\{Mo_8\}_{14}\{Mo_2\}_{14}\{Mo_1\}_{14}$	$\{Mo_8\} = \{(Mo)Mo_5\}\{Mo\}_2$
$\{Mo_{176}\}$	$\{Mo_8\}_{16}\{Mo_2\}_{16}\{Mo_1\}_{16}$	$\{Mo_8\} = \{(Mo)Mo_5\}\{Mo\}_2$
$\{Mo_{368}\}$	$\{(Mo)Mo_5\}'_8\{(Mo)Mo_5\}''_{32}\{Mo_2\}'_{16}\{Mo_2\}''_8\{Mo_2\}'''_8\{Mo\}_{64}$	

cluster anions containing two or three of these units. The structure of $\{Mo_{17}\}$ unit can be reduced to two $\{Mo_8\}$-type group linked by $\{Mo_1\}$-type unit. The $\{Mo_8\}$ building block is found in many other large POMo structures.[47,48] Some of characteristic clusters and the corresponding formulation based on larger and smaller building blocks are presented in Table 3.

Stability of the smaller clusters, determined by the solution conditions, is crucial in the formation of larger cluster such as wheel-shaped cluster $\{Mo_{154}\}$, $\{Mo_{176}\}$ and even more $\{Mo_{248}\}$ cluster. The ring–shaped clusters can act as hosts for smaller polyoxomolybdate cluster, for instance $\{Mo_{36}\}$ unit. The strategy of the formation of large cluster is based on highly negatively charged fragments preventing thus possible degradation and hydrolysis. This is achieved by substitution of metal centers of lower oxidation states for ones of higher oxidation state. Furthermore, increasing the molecular size of the system the multi-functionality can be achieved. For instance in the case of $\{Mo_{57}\}$ cluster it is possible to place or exchange paramagnetic centers like $Fe^{II/III}$ and VO^{II} in the linker position and control magnetic properties.[49] The cavities of the clusters filled with positively charged units can be emptied again by oxidation. These reactions represent a model for uptake and release of metal centers in metal storage proteins under redox–active conditions and for a molecular switch.[50]

A new member of giant polyoxomolybdates is a compound $(NH_4)Na_2[Mo^{VI}_{36}O_{108}(NH_2OH)_2(OH)_6(H_2O)_{12}]\cdot 35H_2O$ containing bridging hydroxylamine molecules. Each giant ellipse-shaped cluster anion $\{Mo_{36}(NO)_2\}$ consists of two large $[Mo_{15}O_{50}(Mo^{VI}O)_2(\mu\text{-}NH_2OH)(\mu\text{-}OH)(OH)_2(OH_2)_6]^{5-}$ units linked together by two MoO_2^{2+} centers. These anions $\{Mo_{36}(NO)_2\}$ are connected *via* distorted monocapped pentagonal-pyramidal sodium in a three-dimensional structure with channels filled with lattice water molecules and $(NH_4)^+$ ions.[51]

A. Müller and collaborators have been described the salt $(NH_4)_{42}[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(H_2OCH_3COO)_{30}(H_2O)_{72}]\cdot$ *ca.* $300H_2O\cdot$ *ca.* $10CH_3COONH_4$, an inorganic super fullerene,[52] with an integrated icosahedron, namely a Keplerate with more than 500 atoms and the highest Euclidian symmetry. The sphere consists of a total of $12\{Mo_{11}\}$-polyoxomolybdate fragments of fivefold symmetry and they are generated from central pentagonal bipyramidal $\{MoO_7\}$ groups (Figure 9).

The ring-shaped mixed-valence polyoxomolybdates of the type $\{Mo_{154}\}$, $\{Mo_{176}\}$ or $\{Mo_{248}\}$ are a new class of giant clusters with nanometresized cavities[53] and interesting for host-guest chemistry. From the wheel-shaped $\{Mo_{176}\}$ cluster the $\{Mo_{248}\}$ cluster can be formed by addition of further units to the inner surface of the $\{Mo_{176}\}$ wheel. The crystal structure of both ring–shaped clusters have practically the same lattice constants and show the same type of packing of the two kinds of clusters having the same diameter. Two $\{Mo_{36}O_{96}(H_2O)_4\}$ units incorporate in such a way that the packing of the wheels is not affected and the structure is extended. The peripheral ring region is built up by $\{Mo_2\}\{(H_2O)(O_{term})_2MoOMo(O_{term})_2(H_2O)\}$, $\{Mo_8\}$ and $\{Mo\}$ units each occuring 16 times. The terminal oxygen atoms have a high electron density and therefore a high affinity for protonation. Thus they are the starting point for the subsequent growth and condensation process.

One of the largest polyoxomolybdates, $Na_{48}[H_xMo_{368}O_{1032}(H_2O)_{240}(SO_4)_{48}]\cdot$*ca.* $1000H_2O$ ($x \approx 16$)[54,55] has a shape of a hedgehog and the size of haemoglobin (diameter approximately 6 nm). This deep-blue compound crystallizes in the space group *I*4mm and the unit cell contains two giant hedgehog-like cluster anions of D_4 symmetry with a central ball-shaped fragment $\{Mo_{288}O_{784}(H_2O)_{192}(SO_4)_{32}\}$ and two capping

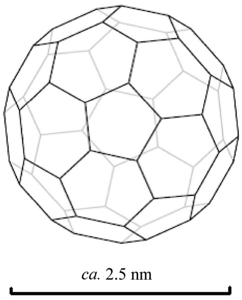


Figure 9. Structure of the icosahedral $\{Mo_2^V\}_{30}$ units with 12 regular pentagons and 20 trigonal hexagons as well as its coherence to the fullerene (adapted from Ref. 52).

units $\{Mo_{40}O_{124}(H_2O)_{24}(SO_4)_8\}$. The cluster can be described as a structure composed by six building blocks, while a giant molecular container with a huge cavity (diameter ≈ 2.5 × 4.0 nm) offers space for a large number of about 400 H_2O molecules. The $\{Mo_{368}\}$ cluster can be visualized as a hybrid between the giant wheel $\{Mo_{176}\}$-type and ball $\{Mo_{102}\}$-type cluster.[56]

The $\{Mo(Mo_5)\}$ and $\{Mo_1\}$ units are found in the ball-type cluster, and $\{Mo(Mo_5)\}$ and$\{Mo_2\}$ units in the wheel-type cluster. The complete knowledge of the $\{Mo_{368}\}$ cluster offers new options of handling the giant clusters as intact units for the preparation of composite materials.

The linking processes follow the well-defined rules and can occur in different phases:[57]

– the linking units must have appropriate well-defined functionalized external and internal surfaces

– wheel and sphere-shaped nanosized molybdenum oxide based clusters fulfil these conditions

– spherical clusters may be linked to form a chain, layers or necklace

– crosslinking of spherical clusters produces the structure with cavities which may host large anions or guest-molecules.

The linking of nanosized clusters present a possibility to prepare a new class of materials with well-defined channel cavities. Some of those nanoclusters are emerging as a novel type of molecular catalysts. The example is nanosized ring-shaped cluster unit forming the compound $Na_{21}[Mo^{VI}_{126}Mo^{V}_{28}O_{462}H_{14}(H_2O)_{54}$-$(H_2PO_2)_7]\cdot 300H_2O$ of 2/m symmetry in which the units are linked through covalent Mo–O–Mo bonds to give a layered structure.[58] The packing of these layers gives rise to nanosized channels with encapsulated $H_2PO_4^-$ ligand and water. It is also possible to replace molecules/ligands at the surface or within the cavities and subsequently change the properties. The other example is the ring-shaped structure of the compound $Na_{21}[Mo_{154}O_{462}H_{14}(H_2O)_{48}(HOC{-}(NH_3^+)HC{-}CH_2{-}S{-}S{-}CH_2{-}CH(NH_3^+){-}COO^-)_{11}]\cdot 250H_2O$ which captures the oxidation product of cysteine.[59]

It is possible to place molecules at the inner wall of the cavity of a giant metal–oxide based wheel cluster by replacing H_2O molecules. With the use of ambiphiling and/or multiphilic ligands new surface structures can be generated. Unusual spherical Mo-oxides $[\{(Mo)Mo_5O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(L)_{30}\}]^{42-}$ (organic molecule or H_2O) open up new techniques in supramolecular nanotechnology by a large number of pores/receptor sites.[60] The compound is analogous of the most simple so-called T = 1 virus type containing 60 proteins. In both cases the 60 $\{MoO_6\}$ units are packed around the fivefold axes. The above spherical cluster with different pore size can act as an effective and specific nanosponge for complementary substrates.

Interesting example is a crown-shaped POMo cluster which can accomodate large metal complexes with organic ligands in its nanocavity to form discrete inorganic/organic nanocomposite material.[61]

Synthesis

A brief compilation of polyoxomolybdate synthesis is presented. Mostly these are common preparative methods in aqueous and nonaqueous solutions. Recent years the hydrothermal synthesis of molybdenum oxide-based materials has attracted considerable attention. The hydrothermal method, though still in the phase of exploration, due to the preparative flexibility offers to control the complex structure-synthesis relationship in materials chemistry.

Synthesis in Aqueous and Non-aqueous Solutions

The most common synthetic method of polyoxomolybdates involves acidification of aqueous solution of simple oxoanions and the necessary heteroatoms. Isolation of the polyanions is generally achieved by addition of an appropriate counterion, such as alkali metal, ammonium or tetraalkylammonium. The recent expansion of the synthesis of polyoxomolybdates is also a consequence of their solubility in different organic solvents displaying thus characteristic metal-ligand reaction chemistry. The chemistry of such polyoxomolybdates in non-aqueous solvents has been characterized by the replacement of peripheral oxo-groups by organic ligands with O– and N– donors or different inorganic ions as ligands.

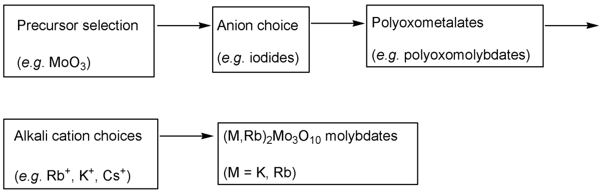
Synthesis of molybdenum(VI) complexes with oxalate ligands are of continuing interest due to their use in analytical chemistry and industry in spite of numerous complexes known for many years. A number of new molybdenum(VI) oxalate complexes with a smaller number of building blocks were prepared from a mixture of molybdenum(VI) oxide, pyridine, HCl and equivalent amounts of oxalic acid dihydrate.[18] The addition of tetramethylammonium chloride or γ-picoline to the mixture resulted in two more oxalato complexes. The mixing of molybdenum(VI) oxide, oxalic acid dihydrate and ammonium chloride resulted in the molybdenum(VI) complex with interesting intermolecular hydrogen bonds within the dimeric anion.[15,16] Furthermore, the reaction of molybdenum(VI) oxide with oxalic acid or alkali oxalate and alkali halides gives two series of Mo^{VI} oxalate complexes containing Mo_2O_5 and MoO_3 core, respectively.[17]

Synthesis and characterization of acetato complexes of molybdenum(IV), (V) and (VI) in the mixture of appropriate molybdenum precursors, acetic acid and acetic acid anhydride are of interest to understand the reaction of $(\mathrm{MoO_4})^{2-}$ with an excess of acetic anhydride. The characterization of the products helps to explain how the reduction of molybdenum depends upon the reaction conditions, reducing agent and starting components.[19] In order to understand the role of molybdenum as a catalyst in the esterification reactions the polyoxomolybdate complex with smaller number of building blocks $(\mathrm{Mo_4O_{10}})$ was prepared from molybdenum(VI) compound, methyl ester of 2-hydroxynicotinic acid in a methanol suspension.[24] Hexamolybdate anion $(\mathrm{Mo_6O_{19}})^{2-}$ incorporated in the structure of bis(tetramethylammonium)hexamolybdate hydrate is obtained from a mixture of $\mathrm{MoO_3}$ in water, glycine and tetramethylammonium salt.[62] The same $\mathrm{MoO_3}$ oxide was also used in the mixture with $\mathrm{H_2SO_4}$ and dimethylethylenediamine to obtain $(\mathrm{Mo_8O_{26}})^{2n-}$ anion.[37]

A novel class of POMs with two kinds of polyoxomolybdate anions: $(\mathrm{Mo_6O_{19}})^{2-}$ and $(\mathrm{Mo_8O_{26}})^{4-}$ have been sythesized as a rare example with two kinds of anions. The compound was prepared by the reaction of Bismarck Brown Y *N*,*N*'-dicyclohexylcarbodiimide and $(\mathrm{Bu_4N})_4[\alpha\text{-}\mathrm{Mo_8O_{26}}]$ in anhydrous acetonitrile under nitrogen.[39] Recently a mixed valence cluster anions of $\mathrm{Mo^V}$ and $\mathrm{Mo^{VI}}$ were prepared. Such cluster comprises a type of polyoxommolybdate cluster framework that displays an unprecedent topology and high negative charge and nucleophilicity. These complexes are obtained from the solutions by changing the reaction conditions and reaction components. The building blocks can link to larger aggregates.[43,44,63]

Aqueous synthesis under different boundary conditions offers a strategy for the formation of complex molecular systems by linking a large number of molybdenum oxide building blocks. The size and shape of clusters can be controlled generally by acidity of the reaction medium.[64] Such giant polyoxomolybdate anions can contain bridging hydroxylamine moities.[51] By performing the synthesis in aqueous solution of $\mathrm{Na_2MoO_4}$, hypophosphorus acid and in the presence of electrolyte salt nanosized ring-shaped layered multifunctional structures are generated with $\mathrm{Mo^{VI}_{126}}$ and $\mathrm{Mo^{V}_{28}}$.[58,65] When an aqueous solution of ammonium molybdate is reduced to medium ratios of $\mathrm{Mo^V/Mo^{VI}}$ at given pH values, $\mathrm{MoO_7}$ is generated and stabilized by acetate ligand and the spherical anion is formed in organized shape such as super fullerene.[52] Strictly controlling $(\mathrm{MoO_4})^{2-}$ solution with the acid, compounds with giant mixed valence cluster anions of sphere or hedgehog shape containing 368 Mo atoms can be prepared.[54,55] In an acidified aqueous $(\mathrm{MoO_4})^{2-}$ containing solution with an appropriate reducing agent and controlled pH ring, tube or wheel shaped self-assemlies containing $\mathrm{Mo_{154}}$ to $\mathrm{Mo_{248}}$ clusters are synthesized.[53,66]

Hydrothermal/Solvothermal Synthesis
Hydrothermal method appears as a very powerful and flexible synthetic method in inorganic chemistry (Scheme 1) ranging from nanoparticles, mesoporous compounds to single crystals with cm-dimensions.[22,67,68]



Scheme 1. Systematic hydrothermal pathway to new alkali trimolybdates.

The reaction parameters in the closed autoclave system at elevated temperatures, which determine complex structure-synthesis relationship, are still in the process of exploration. Polyoxomolybdates and polyoxomolybdovanadates due to the ability to form a large number of structures, represent a good framework for hydrothermal synthesis. A number of POMs have been prepared by hydrothermal and solvothermal method so far starting with smaller building blocks to nanostructures.[20,25,36,69] A novel polyoxomolybdate-based organic inorganic complexes with $\mathrm{Mo_6}$ and $\mathrm{Mo_8}$ building blocks synthesized by the same method represent the first example of racemic complexes.[38] Similarly molybdenum complex with organic ligands (*e.g.* nicotinic acid) with a 3D supramolecular architecture was isolated.[34] The complexes which present novel examples of assembling the oxomolybdate under hydrothermal conditions are isolated. The variation in the structure is a consequence of the differences in the conectivity between the $(\mathrm{Mo_8O_{26}})$ cluster.[41]

Functionalization of POMo
Functionalization of polyoxomolybdates *i.e.* the replacement of one or several oxo ligands by other ligands, provides molecular model for selective oxidation and a route to their application in catalysis, medical application and supramolecular chemistry. Organic ligands may also stabilize some unstable species. A tetranuclear oxomolybdenum(V) complex with bridging squarate ligands were synthesized from $\mathrm{Na_2MoO_4\cdot 2H_2O}$ in acidic water solution.[23]

Functionalization of $(\mathrm{Mo_6O_{19}})^{2-}$ anion was performed in the reaction mixture with $\mathrm{Ph_3{=}NPh}$ in anhydrous pyridine.[9] A convenient method for the systematic introduction of a variety of organoimido ligands at terminal oxo sites in the hexamolybdate cluster was

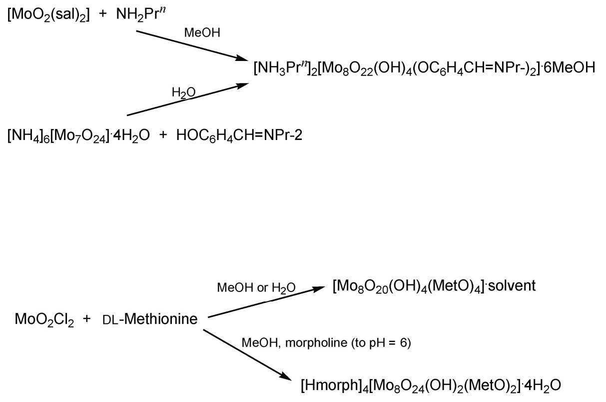
$$[(CH_3CH_2CH_2CH_2)_4N]_2[Mo_6O_{19}] + RNCO \xrightarrow{py} [(CH_3CH_2CH_2CH_2)_4N]_2[Mo_6O_{18}(NR)] + CO_2$$

R = alkyl or aryl substituent

Scheme 2. Substitution of imido ligand into a hexamolybdate complex.

proposed. The reaction was performed in the mixture of hexamolybdate ion and the various isocyanates in pyridine solution (Scheme 2).[8]

Several substituted octamolybdates anions $(Mo_8O_{26}L_2)^{2n-4}$ with 16 terminal positions, two of which are occupied by the ligands, were described starting from the $[MoO_2(sal)_2]$ (salH = salicylaldehyde) and MoO_2Cl_2 in methanolic solution or water (Scheme 3).[33]



Scheme 3. Substitution reactions into octamolybdate anions (adapted from Ref. 33).

A series of aryldiazenido compounds with $(Mo_6O_{18})^{2-}$ anion were functionalized in acetonitrile or in methanol. The ligands in these isostructural compounds can act as π-donor or/and π-acceptor ligands.[27]

It has been shown recently that the γ-type octamolybdates coordinated by DL-alanine or glycilglycine prepared in aqueous solution of Na_2MoO_4 depending on the acidification agent, exhibit biological activities, namely antitumor activity.[31]

POLYOXOMOLYBDOVANADATES

Characteristic Structures

Contrary to the numerous well explored polyoxomolybdates relatively little is known about the structures of polyoxomolybdovanadates. Mo^{VI} and V^{V} have similar ionic radii (0.73 and 0.68 Å) and coordinations, thus a variety of combinations of the compositions and structures of the oxometalate anions could be expected. They are mostly molybdenum- or in some cases vanadium-rich polyoxometalates.

The compound $[N(CH_3)_4]_4(H_2MoV_9O_{28})Cl\cdot 6H_2O$ is an interesting example with only one Mo atom.[70] The anion displays the structure of the decavanadate with the Mo atom substituted at one «capping» vanadim site. Owing to the 2/m symmetry of the anion the Mo atom is randomly distributed over four «capping» metal atom positions. All metal-to-metal distances vary from 3.065 to 3.207 while the V–O distances within VO_6 octahedra are also similar to those already observed and depend upon the type of oxo ligand. The protonation was assigned to the triply-bridging oxygen atoms, while the doubly-bridging oxygens are a second choise and are protonated to a lesser extent. The Mo–O bond number within the $(Mo/V)O_6$ octahedron amounts 5.25, the theoretical value required for the positions occupied by vanadium and molybdenum in the ratio 3 : 1.

$(Hmorph)_6(Mo_4V_5O_{27})Cl\cdot H_2O$ (morph = morpholine) is a first example of this type molybdovanadates obtained from aqueous solution.[10] The compound is a hybrid of the decavanadate structure in the vanadium-rich region and the β-octamolybdate structure in the molybdenum-rich region. It is built up of nine edge-sharing MO_6 octahedra but with a random distribution of Mo and V atoms in two «capping» metal atom sites in the vanadium–rich region. Since the ratio Mo/V is 4/5, the anion is asymmetrical indicating that the crystal structure contains a statistical distribution of two chiral $(Mo_4V_5O_{27})^{5-}$ anions (Figure 10).

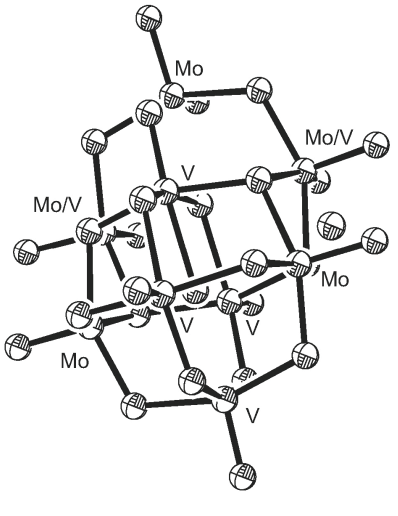


Figure 10. View of $(Mo_4V_5O_{27})^{5-}$ anion (adapted from Ref. 10).

The distortion of the octahedra is significantly greater for MoO_6 than for VO_6. The protonation scheme is also interesting. Whereas in the molybdenum-rich region both terminal and doubly-bridging oxygen atoms are protonated, in vanadium-rich region only doubly and triply-bridging oxygen atoms are protonated. Such a hydrogen bond scheme is a result of the sequence of the negative charge on the oxygen atoms, as well as of the steric effects of the large morpholinium cations and crystal structure packing.

The polyoxo anion $[Mo_6V_2O_{26}]^{6-}$ found in $K_6[Mo_6V_2O_{26}]\cdot 4H_2O$[71] is isostructural with the β-octamolybdate $[Mo_8O_{26}]^{4-}$ anion[72] and with the β-hexamolybdodivanadate in the mixed potassium sodium salt $K_5Na[Mo_6V_2O_{26}]\cdot 4H_2O$.[73]

The compound $(Hmorph)_6[(V^{IV},V^{V},Mo_{10})\text{-}VO_{40}]\cdot 3H_2O$[74] also contains morpholinium cations but higher ratio of Mo/V atoms. The molybdovanadate anion adopts the well known Keggin structure with a V^VO_4 tetrahedron at the centre of 12 surrounding MO_6 octahedra with a random distribution of $10Mo^{VI}$, one V^{IV} and one V^V ions between 12 metal atom positions (Figure 11).

Three MO_6 octahedra sharing common corners form a (M_3O_{13}) group. Four such groups linked together by sharing common edges form the structure of the anion. All hydrogen atoms from the morpholinium-NH_2 groups participate in the hydrogen bonding between cations, molybdovanadate anions and water molecules.

Several molybdovanadates with coordinatively bound oxalato ligands were described in the literature, *e.g.* $(NH_4)_6[Mo_6V_2O_{24}(C_2O_4)_2]\cdot 6H_2O$ and $(NH_4)_4\text{-}[H_2Mo_2V_2O_{12}(C_2O_4)_2]\cdot 2H_2O$.[75] The molybdovanadate anion $[Mo_6V_2O_{24}(C_2O_4)_2]^{6-}$ is composed of six MoO_6 and two VO_6 edge-sharing octahedra of the γ-$(Mo_8O_{26})^{4-}$ type structure. The centrosymmetric tetranuclear anion $[H_2Mo_2V_2O_{12}(C_2O_4)_2]^{4-}$ adopts the structure with a (M_4O_{16}) core typical for both molybdate-ligand and vanadate-ligand system. Bidendate oxalato ligands in both complexes are bonded to the vanadium ions and in both crystal structures molybdovanadate anions are interconnected by numerous hydrogen bonds through ammonium ions and water molecules. The third molybdovanadate compound coordinated by oxalato ligands, $K_6[Mo_6V_2O_{24}(C_2O_4)_2]\cdot 6H_2O$ reveals centrosymmetric molybdovanadate anion which consists of six MoO_6 and two VO_6 edge-sharing octahedra to give the γ-$(Mo_8O_{26})^{4-}$ structure.[76]

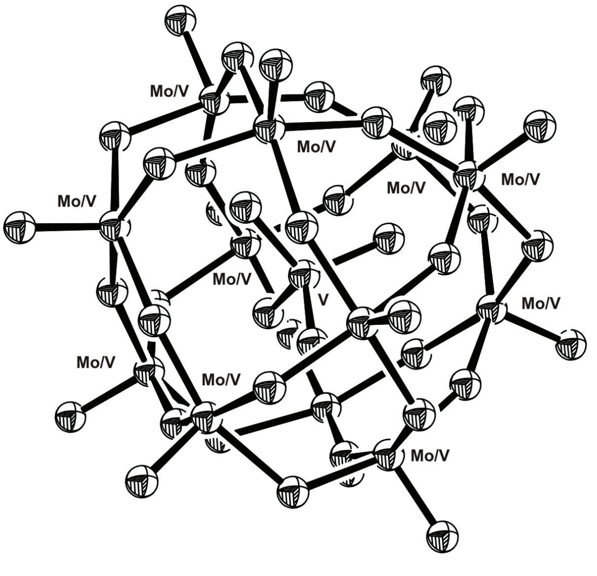


Figure 11. Structure of the molybdovanadate $[(V^{IV},V^{V},Mo_{10})\text{-}VO_{40}]^{6-}$ anion with the surrounding morpholinium cations and water molecules (adapted from Ref. 74).

The first example of a molybdovanadate coordinated by an amino acid (glycine), was $K_2[HMo_6^{VI}\text{-}V^VO_{22}(NH_3CH_2COO)_3]\cdot 8H_2O$.[77] The molybdovanadate anion is built up of six MoO_6 edge-sharing octahedra connected into a ring centered by a VO_4 tetrahedron. The MoO_6 octahedra are in pairs bridged by glycine through its carboxylato group.

Neutral heteropolyoxometalates $[Mo_7^{VI}Mo^{V}V_8^{IV}\text{-}O_{40}(PO_4)]M(phen)_2(OH)_2]_2[M(phen)_2(OEt)]_2\cdot xH_2O$ (M = Co, Ni) are novel windmill-like trimetalic nanoclusters.[78] The mixed molybdenum-vanadium polyoxoanion $[Mo_7^{VI}Mo^{V}V_8^{IV}O_{40}(PO_4)]^{4-}$ exists in both complexes acting as a bridge to covalently link two pairs of transition metal complex fragments. Each vanadium atom exhibits a distorted VO_5 square pyramidal environment, and eight vanadium atoms form a central belt by sharing edges of VO_5 square pyramids. There are two $\{Mo_4O_{18}\}$ rings bonded above and below this V_8 belt. The hydrogen bonds between the lattice water molecules play an important role in stabilizing the molecule in crystal structure. The complexes represent the first example of zero-dimensionality neutral mixed molybdenum-vanadium polyoxometalates with covalently bonded transition metal complex fragments. In the reaction of molybdenum(VI) oxide and ammonium vanadate the triclinic $K_8[Mo_8(V^{IV})V_4O_{40}]\cdot 10H_2O$ (**1**) and monoclinic $K_8[Mo_8(V^{IV})V_4O_{40}]\cdot 9H_2O$ (**2**)[79] were obtained. The structure of the same anion $[Mo_8(V^{IV})V_4O_{40}]^{8-}$ in both compounds is based on the central VO_4 tetrahedron surrounded by a puckered ring of eight edge-sharing MoO_6 octahedra with four VO_4 tetrahedra filling the gaps between the pairs of octahedra. The ESR spectra confirm that the compounds contain one V atom in the reduced +4 state. The bond strength calculations indicate that this extra electron is delocalized over four peripheral vanadium ions. The polyoxomolybdovanadate anions in both structures are interconnected by potassium ions and water molecules resulting in a very complicated three-dimensional network in the crystal structure.

Polyoxomolybdovanadates in a form of α-Keggin fragments can be linked to chains and the compound $[(H_2en)_3H_3O][Mo_8V_4O_{36}(VO_4)(VO)_2]\cdot 4H_2O$ (en = ethylendiamine) is one example of this bicapped α-Keggin fragment. The $\{Mo_8V_7O_{42}\}$ units linked together through V–O–V bonds forming an infinite 1D structure.[80] Its structure consists of one $(Mo_8V_7O_{42})^{7-}$ polyanion, three ethylenediammonium cations, one proton hydrate and four water molecules. The polyanion of the chain is composed by *trans*-vanadium capped α-Keggin unit. The Keggin structure is based on a central V^VO_4 tetrahedra surrounded by $12MO_6$ (M = Mo or V) octahedra arranged in four groups of three edge–shared octahedral (M_3O_{13}). These groups are linked by sharing corners to each other and to the central V^VO_4 tetrahedron. The analogous chain structure with the unusual Mo/V polyoxometalate shows the compound $Na_{0.5}K_{6.5}[Mo_8^{VI}V_4^{IV}O_{36}(V^VO_4)(V^{IV}O)_2]\cdot 12.5H_2O$.[81] The structure of basic anionic unit is described as follows: four Mo^{VI} centers of an α-Keggin type $[Mo_{12}^{VI}O_{36}(V^VO_4)_4]^{3-}$ species are replaced by V^{IV} centers giving a «layered» type structure formed by the different metal atoms. The $V^{IV}\cdots V^{IV}$ distance between atoms within each layer is 5.1 Å and *ca.* 11 Å between layers in adjoining units. This enables exchange interactions interesting in the magnetochemistry.

The compounds $K_3(VMo_{12}O_{40})\cdot 19H_2O$ and $[Ni(H_2O)_6](H_3PMo^VMo_{11}^{VI}O_{40})_2\cdot 30H_2O$ also contain Keggin-type heteropolyanions.[63] In the first molybdovanadate each Keggin-type polyanion is capped and linked by six potassium ions to form extended three–dimensional polymeric structure by the build up of $\{K_3[VMo_{12}O_{40}]\}_n$. This confirmed that the templating effects of cations play an important role in the formation of polymers. The second molybdovanadate, $[Ni(H_2O)_6](H_3PMo^VMo_{11}^{VI}O_{40})_2\cdot 30H_2O$, exhibits discrete Keggin-type structure, in which each heteropolyanion contains one reduced Mo^V atom. Ni^{II} coordinated by six water molecules as the counter cation balances the negative charge of the molecule.

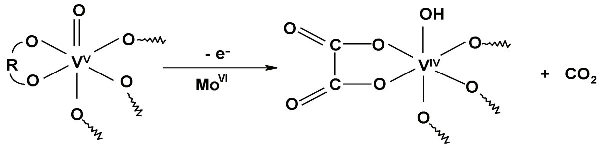
The compound $[NH(CH_2CH_2OH)_3]_6(V_2Mo_{18}O_{62})\cdot$ *ca.* $3H_2O$ is the first example of polyoxomolybdovanadate with the unpredicted composition of V/Mo = 2 : 18,[82] and $(V_2Mo_{18}O_{62})^{6-}$ anion based on V^VO_4 tetrahedra reveals a conventional Dawson structure. The polyanion consists of eighteen $Mo^{VI}O_6$ octahedra forming two (Mo_3O_{13}) and six (Mo_2O_{10}) units which are linked to each other by point-sharing and together surround two V^VO_4 tetrahedra. Recently obtained and structurally characterized polyoxomolybdovanadate $[Co(C_2N_2H_8)_3]_4[Mo^VMo_{14}^{VI}V_{16}^{IV}O_{80}(PO_4)_2]\cdot 10H_2O$ contains two types of heteropoly anions: tetra-capping Keggin anions and hexadeca-metal host shell anions.[83] Another two-dimensional mixed polyoxomolybdovanadate complex $[PMo_8^{VI}Mo_4^{V}O_{40}(V^{IV}O)_2\{Co(phen)_2\}_2](H_2O)$ (phen = phenanthroline) exhibits two distinct $[PMo_{12}V_2O_{42}]$ clusters.[84] One is covalently linked by $[Co(phen)_2]^{2+}$ cation to form 2D cationic sheets $[PMo_8^{VI}Mo_4^{V}O_{40}(V^{IV}O)_2\{Co(phen)_2\}_2]^+$, the other supports two $[Co(phen)_2(\{Co(phen)_2\}H_2O)]$ complexes as heteropolyoxo anion $[PMo_4^{VI}Mo_8^{V}O_{40}(V^{IV}O)_2\{Co(phen)\}_2(H_2O)_2]^{3-}$ forming 3D supramolecular framework. The basic building unit $(PMo_{12}V_2O_{42})$ is built on the well-known α-Keggin structure with two additional five-coordinating terminal {VO} units. Each basic building unit acts as multidendate ligand covalently bonded to $\{Co(phen)_2(H_2O)\}$ or to $\{Co(phen)_2\}$ subunits, respectively. All V atoms are in the +4 oxidation states, 4 Mo atoms within the cluster are in the +5 oxidation states and the remanent 8 Mo atoms in the +6 oxidation states, while in the cluster anion 8 Mo atoms are in the +5 oxidation states and the remainder are the +6 oxidation states. The compound exhibits antiferromagnetic interactions.

Among the organic-inorganic hybrid materials polyoxomolybdovanadate bearing transition metal complexes reveal interesting crystal structures and magnetic properties.[85] For example, these are the bi- and the tetra-capped Keggin anion-supported cobalt-phenanthroline complexes $[\{Co(phen)_2(H_2O)\}_2PMo_{10}^{VI}V_4^{IV}O_{42}][\{Co(phen)_2\}_2PMo_8^{VI}Mo_2^{V}V_4^{IV}O_{42}]\cdot 4H_2O$[86] (**1**) and $[Co_2(phen)_2(OH)_2(H_2O)_4]_{0.5}[\{Co(phen)_2(H_2O)\}_2AsMo_6^{VI}Mo_2^{V}V_8^{IV}O_{44}]\cdot 2H_2O$ (**2**) and the bicapped Keggin anion-based nickel-phenanthroline compound $[Ni(phen)_2H_2O]_2[AsMo_{11}^{VI}Mo^V(V^{IV}O_2)_{0.5}]\cdot 2H_2O$ (**3**). The compound **1** consists of a bicapped anion $(PMo_{10}^{VI}V_4^{IV}O_{42})^{3-}$ supported by two $[Co(phen)_2(H_2O)]$ fragments through its terminal oxygen atoms of the two capping V atoms at the opposite sites. All polyanions constitute an anionic layer, while all the polycations are linked to form a cationic layer by the hydrogen bonding. The compound **2** has two types of free complex cation $[Co_2(phen)_2(OH)_2(H_2O)_4]^{2+}$ in different orientations in the crystal structure and these free cations coexist in the space between polyoxometalate clusters. In the similar compound **3** the Keggin unit is bicapped instead of tetra-capped. Each $(AsMo_6^{VI}Mo_2^{V}V_8^{IV}O_{44})^{5-}$ unit has strong covalent interactions to two $\{Co(phen)_2(H_2O)\}$ units in **2**. Two types of free complex cations of the large volume packed in the space between polyoxoanion clusters are attributed to the supramolecular interactions between phenanthroline rings. Furthermore, **2** contains strong hydrogen bonding interactions between the terminal oxygen atoms of polyanions and the oxygen atoms from ligand water molecule coordinated to the Co atoms. The extensive hydrogen bonding leads to the formation of a chain structure. The structure of **3** consists of bicapped polyoxoanion $[AsMo_{11}^{VI}Mo^{V}(V_{0.5}^{IV}O)]^{4-}$ supported by two $[Ni(phen)_2H_2O]^{2+}$ cations and two lattice water molecules. The $[AsMo_{11}^{VI}Mo^{V}(V_{0.5}^{IV}O)]$ unit as in other bicapped structure contains twelve MoO_6 octahedra and a AsO_4 tetrahedron at the center with two {VO} square pyramidal capping on the opposite sites of the α-Keggin core $\{AsMo_{11}^{VI}Mo^{V}O_{40}\}$. Two bridge oxygen ligand shared between two Co^{II} ions, and Mo^{V} and V^{IV} atoms also linked by bridge oxygen ligands offer a possible route for antiferromagnetic coupling interactions.

Synthesis

Polyoxomolybdovanadates are prepared in a similar manner such as polyoxomolybdates. Oxo-anions of both molybdenum and vanadium are mixed in aqueous or nonaqueous solutions in the presence of acid or base. The complexes are mostly molybdenum-rich molybdovanadates. In a typical reaction between molybdenum(VI) oxide and ammonium vanadate ion in aqueous solution by adding potassium hydroxide two compounds with $[Mo_8(V^{IV})V_4O_{40}]^{8-}$ anion were precipitated. The polyoxomolybdovanadate anions in both structures are interconected by potassium ions and water molecules.[79] In the aqueous mixture of MoO_3 and NH_4VO_3 a morpholine is added. The compound with central tetrahedral V^{V} atom is formed, while the other two vanadium atoms are crystallographycally disordered over 12 MoO_6 octahedral sites $(Hmorph)_6[(V^{IV},V^{V},Mo_{10})VO_{40}]\cdot 3H_2O$.[74] Molybdovanadates with vanadium-rich polyanion have been synthesized from ammonium vanadate and molybdenum(VI) oxide in acidic aqueous solution by adding tetramethylammonium chloride. This is the first example of molybdovanadate that is dominant in aqueous solution.[70] The vanadium–rich compounds with the asymmetric anion $(Mo_4V_5O_{27})^{5-}$ was prepared from the same precursors in acidic aqueous solution and morpholine addition.[10]

Although many different species of molybdovanadates exist in aqueous solution their formation and crystal composition strongly depend upon the metal ions concentration, the range of pH and the time and temperature rather than the relative stability of the species in solution. Water suspension of Mo^{V} and V^{V} oxides in the presence of ammonium oxalate results in two complexes with coordinatively bound oxalato ligands.[75] Similary polyoxomolybdovanadate complex with oxalato ligands is obtained in the suspension with ascorbic and tartaric acid. Both acids were converted into oxalate indicating thus the catalytic role of molybdenum (Scheme 4).[76]



Scheme 4. Proposed reaction mechanism of conversion ascorbic or tartaric acid to oxalate (R = tartaric or ascorbic residues).

Suspension of MoO_3, V_2O_5 and glycine in water at elevated temperature resulted in a new complex of polyoxomolybdovanadate coordinated by glycinato ligand.[77] In acidified aqueous solution of Na_2MoO_4, NH_4VO_3 and a rather high concentration triethanolamine a conventional Dawson structure polyoxomolybdovanadate cluster anion based on VO_4 tetrahedra was isolated, $[Mo_{18}O_{54}(VO_4)_2]^{6-}$.[82]

Prolongated photolysis of aqueous solution containing $(V_4O_{12})^{4-}$ and K_2MoO_4 at pH = 5.5 resulted in the mixed-valent polyoxomolybdovanadate cluster, $K_6H_2[V_8^{IV}V_{14}^{V}O_{54}(MoO_4)]$.[87] These type of reactions allows the preparation processes to be easily controlled and provides many opportunities to prepare mixed valence PMOs, such as spherical polyoxomolybdovanadates described by M. T. Pope.[88]

The hydrothermal synthesis enables preparation of a number of complex organic-inorganic hybrid materials of polyoxomolybdovanadates with different Mo oxidation states and a formation of new 3D supramolecular structures.[84,85] The preparative flexibility of hydrothermal synthesis was demonstrated in the preparation of polyoxomolybdovanadate clusters with various complex structures. A mixture of V_2O_5, MoO_3, ethylenediamine and water was treated hydrothermaly at 140 °C in the autoclave. The reaction resulted in the polyanion chains constructed by *trans*-vanadium capped α-Keggin fragment $\{[Mo_8V_4O_3(VO_4)(VO_2)]_n\}^{7-}$ anion.[80] During the hydrothermal synthesis many factors such as stoichiometry, acidity, temperature, pressure and time have a great influence on the compounds. By mixing NH_4VO_3 and $H_2MoO_4\cdot 2H_2O$ with the addition of 1,10-phenanthroline and ethanol, depending on the reaction condition two *windmill*-complexes with $[Mo_7^{VI}Mo^{V}V_8^{IV}O_{40}(PO_4)]^{4-}$ polyoxoanion were obtained.[84] Mixed Mo/V metal-oxygen cluster compound containing the two types of typical heteropoly anions was prepared from V_2O_5, $CoCl_2$, Na_2MoO_4, ethylene-diamine and water.[83]

APPLICATION OF POLYOXOMETALATES

Heteropoly- and isopolyoxometalates offer extreme variabilities of molecular compositions, size, shape and charge density which determine their properties and applications. Generally, the application of polyoxometalates is centered on their redox properties and their high charges. The majority of the literature and patents of about 85 % are found in the area of catalysis.[89] The remaining applications cover analytical chemistry, electrochemistry, clinical analysis, sensors, medicine and other fields. The application of POMs in different areas of chemistry, medicine and technology is well and comprehensively surveyed up to 1998 in Chemical Reviews.[5] Polyoxomolybdates and polyoxomolybdovanadates are part of this application. The research in this field is still growing due to the new synthesis of complex structures with controlled properties. Therefore, in this presentation only recent results including polyoxomolybdates and polyoxomolybdovanadates are reviewed. Polyoxomolybdovanadates are of special interest as redox catalysts. Their reoxidation by molecular oxygen resulted in their use in a variety of oxidation reactions.[76]

Recently obtained polyoxomolybdates containing tris(hydroxymethyl)aminoethane have shown substantial catalytic activity toward the reduction of bromate and weak activity toward chlorate.[90] In order to apply eco-friendly, recyclable and inexpensive catalyst vanadium(V)-substituted polyoxomolybdates (series of $[H_{3+x}PMo_{12-x}V_xO_{40}]$, $x = 1–3$) have been used as a catalyst for regioselective nitration of phenol.[91] The effects of various parameters such as concentration of phenol, solvent, temperature and time reaction on the catalytic process were examined in details considering the yield and selectivity.

One of the most attractive application of POMs is in medicine. They have been known for their antitumoral, antiviral and antibiotic activity. This activity is ascribed to the advantageous feature of POMs that nearly every molecular property that impacts the recognition and reactivity of those complexes with target biological macromolecules can be altered. A number of new compounds functionalized with organic or biological groups increase bioavailibilities and enhance the recognition of biological targets. However, POMs have a principal disadvantage in the medical use since they are not organic species which dominate in the pharmaceutical industry. Though the number of papers on potential applications of POMs have been published to date including excellent reviews,[5,12] further knowledge regarding structure–activity behaviour *in vivo* is needed. This information is crucial in the design of better drugs. Last few years there is a growing interest in biological activity of polyoxomolybdates and their relevance in medicine. The first report describing the antitumoral activity of heptamolybdate and the corresponding mechanism was proposed by Yamase.[92] Some domaines in tumor cells reduce heptamolybdate(VI) to heptamolybdate(V), while the other domaines reoxidize $[Mo_7O_{23}(OH)]^{6-}$ back to $(Mo_7O_{24})^{6-}$.

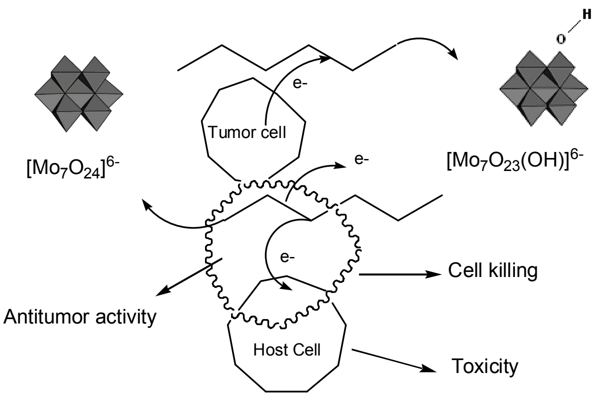
$$(Mo_7O_{24})^{6-} + 1e^- + H^+ \rightarrow [Mo_7O_{23}(OH)]^{6-}$$

Reduced form Mo^V is highly toxic leading to the specifity of tumor cell killing. This results indicated that the structure of the $(Mo_7O_{24})^{6-}$ is important for antitumor activity. Polyoxomolybdate, namely the structure of $(Mo_7O_{24})^{6-}$ has been recognized as one of significant antitumoral polyoxomolybdate (Scheme 5).

Polyoxomolybdate $(NH_3Pr^i)_6(Mo_7O_{24})\cdot 3H_2O$, with the characteristic heptamolybdate anion inhibited the cell growth of human pancreatic cancer. It is suggested that the anti-tumor activity of the complex results from the activation of the apoptotic pathway and that the mechanism differs from that of conventional antitumor agents and thus may be effective in treating pancreatic cancer.[93] The same heptamolybdate anion was used to perform anti-tumor tests in MKN45 cells (human gastric cancer line in nude mice).[94]

Above mentioned polyoxomolybdate did not induce any adverse effects such as body weight loss in the host mice. It has also shown the growth suppression against several tumors, for example Co-4, human colon cancer, MX-1, human brest cancer and OAT, human lung cancer.[95] The compound is water soluble and structurally stable at pH = 5–7. All described characteristics and further analysis of cytotoxicity of polyoxomolybdate *in vivo* model of anti-tumor growth offer a novel development of drug delivery systems using this class of compounds.

Photoreduced compound of $(NH_3Pr^i)_6(Mo_7O_{24})\cdot 3H_2O$ gives the polyoxomolybdate, $(Me_3NH)_6$-$[H_2Mo^V_{12}O_{28}(OH)_{12}(Mo^{VI}O_3)_4]\cdot 2H_2O$. Anti–tumor tests have shown that this polyoxomolybdate is a novel effective reagent in treating pancreatic cancers. The research continues in *in vivo* models.[96] Polyoxomolybdates are



Scheme 5. Proposed mechanism of the antitumor activity of $(Mo_7O_{24})^{6-}$ (adapted from Ref. 4).

known to hydrolyze adenosine triphosphate, ATP, and the reactivity towards ATP has been implicated as a key in their anti-cancer activity. ATP hydrolysis in the presence of polyoxomolybdates at different pH levels has been investigated with a help of ^{31}P NMR, ^{1}H NMR measurements, high pressure liquid chromatography and isothermal titration calorimetry. Systematic analysis of the ATP hydrolysis products in wide range of pH at 20 °C has revealed at pH levels of 6 and 4 a dominant formation of adenosine diphosphate, ADP, while at pH = 2 ATP was decomposed mainly to adenosine monophosphate, AMT. ATP hydrolysis occurs through the interaction of phosphate sites in the ATP side-chain with molybdate forming $[(PO_4)_2Mo_5O_{15}]^{6-}$-like ATP molybdate complex as an intermediate. Interaction with the adenine ring is also included with an accompanying aggregation of molybdates {aggregated to $(Mo_7O_{24})^{6-}$} at pH = 4.

Functionalization of polyoxomolybdates with amino acids or peptides may help to modify biological properties of complexes and induce novel synergic effects. However, there are very few complexes with covalently bound aminoacids.[31,59,98] γ-octamolybdates with coordinated amino acids and peptide molecules were tested on antitumor activity. Based on *in vitro* screening results of all tested compounds showed a differential cell-growth inhibition in a dose–dependent manner selectively on HepG2 and MCF-7 cell lines. It is however possible that the octamolybdate framework is fully or partially dissociated and the products may be responsible for the observed antiproliferative activity. Those studies are in progress.[31]

A new complex functionalized with DL–proline ligands was prepared.[32] Two proline ligands are attached to Mo^{VI} ions *via* monodentate coordination of the carboxylate groups, $Na_4[Mo_8O_{26}(proO)_2]\cdot 22H_2O$. The structure of the complex is strongly dependent on the pH values. At physiological pH polyoxomolybdate is completely dissociated into the monomeric $(MoO_4)^{2-}$ units. By the combination of multinuclear NMR spectroscopy the reactivity of the complex towards the hydrolysis of ATP was tested at different pH values. The anti-tumor activity of this type of POM complexes can be related to their reactivity towards the ATP.

Though the biological activity of POMs has been well documented further research and development on their biomedical application opens new possibilities in diagnosis and therapy of diseases. The large POMo clusters are of special interest in the future application as targeted nanosized molecular materials. The ring-shaped and wheel-shaped clusters participate in the formation of nanosized crystalline materials with well-defined cavities and pores. Such porous materials may play a key role in the catalysis and separation methods and may show magnetic properties.[99] Recently discrete inorganic-organic nanocomposite material has been reported.[90,100,101] Spherical-shaped POMo structures are designed so that they behave as an artificial cell/nanochromatograph (AC/NC) towards a wide range of counter cations. The AC/NC can be used to study the complexation behaviour under confined conditions with the possibility to mimic cation transport through biological ion channels including general informations about the transport processes through molecular pores.[102] Further research in the application of POMs presents a challenge for complex chemistry.

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SAŽETAK

Polioksomolibdati i polioksomolibdovanadati – od strukture do funkcije: noviji rezultati

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Autorski revijalni članak daje literaturni pregled važnijih radova u području kemije polioksomolibdata i polioksomolibdovanadata posljednjih dvadesetak godina. Navedena su najznačajnija postignuća u sintezi, određivanju kristalne i molekulske strukture kao i primjeni ove klase spojeva. U prvom su dijelu opisani polioksomolibdati građeni od manjeg broja strukturnih jedinica do novih strukturnih oblika polioksomolibdatnih klustera supramolekulske arhitekture. Nove sintetske metode kao funkcionalizacija i hidrotermalna/solvotermalna sinteza omogućuju kontrolu oblika i veličine nastalih struktura. Sinteza organsko-anorganskih hibridnih spojeva pokazala se najuspješnijom u pripravi novih vrsta materijala. U drugom je dijelu obuhvaćena sinteza i struktura polioksomolibdovanadata s poliokso jezgrama bogatim molibdenom ili vanadijem, miješani vanadij-molibden polioksoanioni s različitim oksidacijskim stanjima metalnih iona i organsko-anorganski hibridni materijali. U trećem je dijelu opisana primjena navedenih spojeva. Funkcionalizacija polioksometalata organskim ligandima čini ove spojeve važnim u području biologije, medicine, katalize i znanosti o materijalima. Razmotren je značaj velikih polioksometalatnih klustera u kemiji nanomaterijala i izazov koji oni predstavljaju za budućnost kemije kompleksa.