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CURRENT ASPECTS OF THE POLYOXOMETALATE/ /METAL OXIDE-BASED CLUSTERS.
II. SPECIAL ASPECTS

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ABSTRACT. Current special aspects of the polyoxometalate/metal oxide-based clusters are presented and discussed.

Polyoxometalate/metal oxide-based clusters with infinite molecules, generated through an inflationary multiplication of a certain discrete molecule, are described and exemplified.

Supramolecular entities that consist of a guest polyoxometalate / metal oxide-based cluster incorporated in the cavity of a larger host polyoxometalate/metal oxide-based cluster are also presented and exemplified.

Eventually, a new complex system of 100 water molecules encapsulated in the internal cavity of the [Mo_{132}] "giant sphere", having the surface pores closed by organic cations, is presented. The probability that this new system with amazing symmetry could open the way towards a new super-supramolecular chemistry is discussed.

The first part of the presentation of certain current aspects of the polyoxometalate/metal oxide-based (POM/MOB) clusters was dedicated to some general aspects [1]. The second part is reserved for the presentation of several special aspects concerning mostly the new generation of these clusters having supramolecular properties.

POLYOXOMETALATE / METAL OXIDE-BASED CLUSTERS WITH INFINITE MOLECULES

The great majority of POM/MOB clusters are discrete/individual molecules, generated by condensation of the corresponding oxoanions. But sometimes the condensation process may continue, resulting eventually in infinite/collective molecules. These infinite clusters are molecular assemblies, generated through an inflationary multiplication of a discrete molecule in one, two or three dimensions, with formation of chain (1D), layers (2D) or networks (3D).

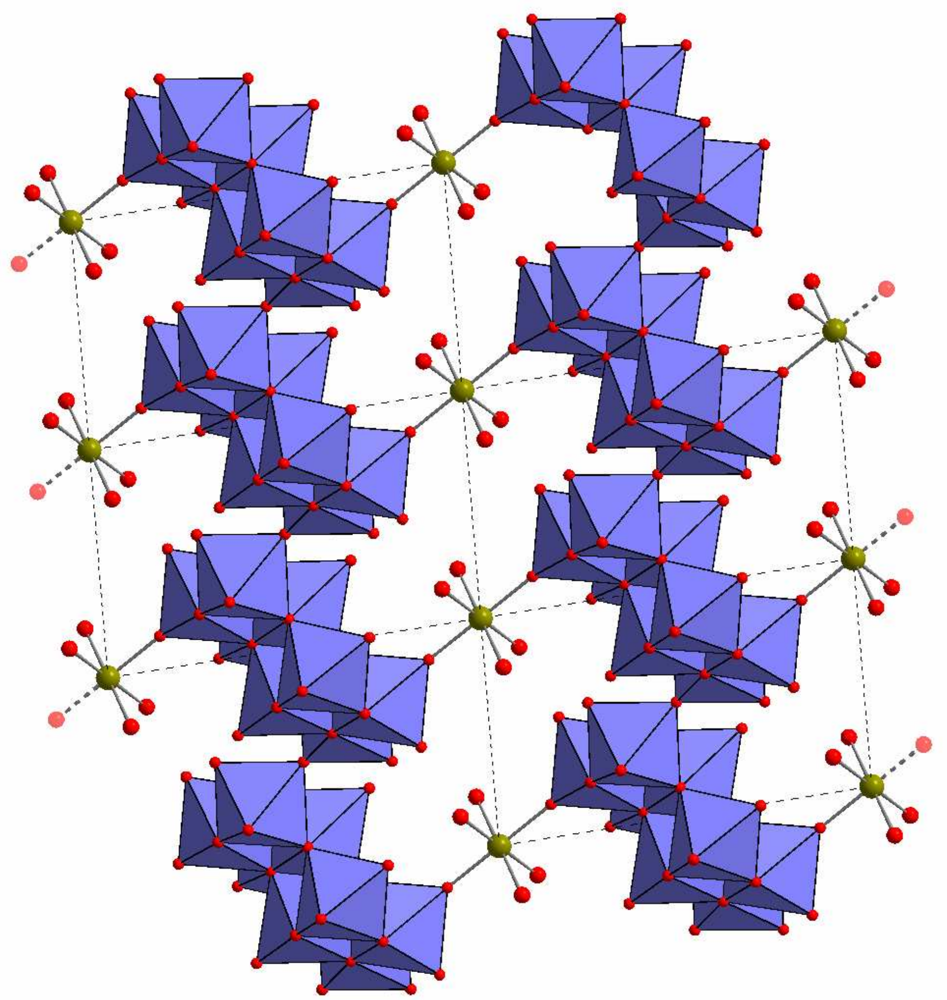


Fig. 1. Section of a $[Fe(H_2O)_4Mo_8O_{27}]_\infty$ layer showing the $[Mo_8O_{27}]^{6-}$ fragments in polyhedral representation and the octahedral Fe^{II} coordination sphere in ball-and-stick representation. The Fe centres form parallelograms in the *ac* plane. Color code: $[Mo_8O_{27}]$ = blue; Fe = yellow; O = red.

We shall illustrate the POM/MOB clusters with infinite molecules by presenting the structure of an interesting layer cluster, not published until now [2].

Initially, the chemical analyses suggested the formula $Na_4[Fe^{II}(H_2O)_4Mo_8O_{27}]\cdot 16H_2O$ for the corresponding neutral compound. But the fact that the compound is insoluble in water indicates a more complex structure. Consequently, the single-crystal X-ray diffraction analysis revealed that the compound and the corresponding POM/MOB cluster have a layer-type structure, composed of $[Mo_8O_{27}]_\infty$ chains cross-linked by partially hydrated Fe^{II} centres.

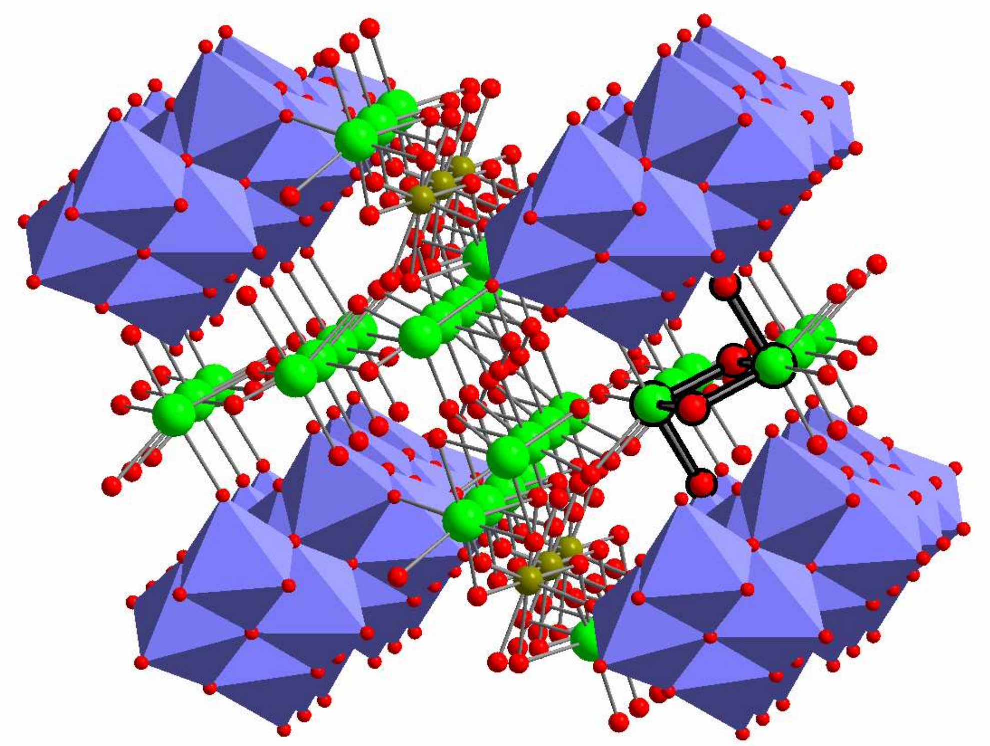


Fig. 2. Linking of two $[Fe(H_2O)_4Mo_8O_{27}]_\infty$ layers (shown as section of each 2 × 3 connected $[Mo_8O_{27}]^{6-}$ fragments) by stacked Na centres. One O-Na-$(H_2O)_2$-Na-O group is emphasized. Color code: $[Mo_8O_{27}]$ = blue; Fe = yellow; Na = green; O = red.

The basic fragment $[Mo_8O_{27}]^{6-}$ is built up of eight MoO_6 edge sharing octahedra. The $[Mo_8O_{27}]^{6-}$ units are linked through bridging O atoms belonging to Mo-O-Mo groups, forming $[Mo_8O_{27}]_\infty$ chains parallel to the crystallographic *a* axis. Each chain is cross-linked to an adjacent chain through Fe-O-Mo bridges, parallel to the *c* axis, thus forming a $[Fe(H_2O)_4Mo_8O_{27}]_\infty$ layer in the *ac* plane. The Fe^{II} centres form intra-layer parallelograms having identical dimensions to those of the parallelograms spanned by the crystallographic a and c axes, see Fig. 1.

It should be also noticed that chains of Na^+ ions based on staggered groups of four Na centres extend parallel to the *c* axis between the layers. Five H_2O ligands and one O atom from a $[Mo_8O_{27}]^{6-}$ unit are linked to each Na centre, which is also connected to an adjacent Na centre through two Na-H_2O-Na bridges and to one $[Mo_8O_{27}]^{6-}$ unit through a Na-O-Mo bridge. This determines additional cross-linking within and between the $[Fe(H_2O)_4Mo_8O_{27}]_\infty$ layers through formal Mo-O-Na-$(H_2O)_2$-Na-O-Mo linkages, see Fig. 2.

The structure of the presented layer cluster with $[Fe^{II}(H_2O)_4Mo_8O_{27}]_\infty$ chains is similar to that of another layer cluster having $[Mn^{II}(H_2O)_4Mo_8O_{27}]_\infty$ chains [3].

PURE SUPRAMOLECULAR POLYOXOMETALATE/METAL OXIDE-BASED CLUSTER ENTITIES

In the first part of the study we underlined that the new generation of the substances under discussion, having only covalent bonds between atoms, can be named POM/MOB clusters with supramolecular properties or pseudo-supramolecular clusters.

On the other hand, the fact that POM clusters have internal cavities which can incorporate/enclose small atoms or molecules (neutral, cationic or anionic), thus building supramolecular entities was well known. For instance, the cage of certain polyoxovanadates acting as host can encapsulate simultaneously cations and anions, such as $[(2NH_4^+, 2Cl^-) \subset V_{14}O_{22}(OH)_4(H_2O)(C_6H_5PO_3)_8]^{6-}$ [4, 5]. The cage of the POM cluster consists of two half-shells formed from isopoly-oxovanadate and phenylphosphonate units. The central guest $(2NH_4^+, 2Cl^-)$ system is a cation/anion aggregate encapsulated within the cavity of the host POM cluster, which is formally separated into two segments by two H_2O molecules bound to V^{IV} centres. The two H_2O molecules stabilize the guest $(2NH_4^+, 2Cl^-)$ system by hydrogen bonds.

But very recent research which started in 2000, led to the synthesis of certain pure POM/MOB clusters which are truly supramolecular, having all the characteristics and properties nominalized for these substances/entities. Thus, several supramolecular entities which consist of a POM/MOB cluster (guest, nucleus) incorporated in the cavity of a larger POM/MOB cluster (host, capsule) have been synthesized.

The first such example is the $[H_xPMo_{12}O_{40}{\subset}H_4Mo^{VI}_{72}Fe^{III}_{30}CH_3COO)_{15}O_{254}(H_2O)_{98}]$ ca. 60 H_2O supramolecular entity, abridged as $[PMo_{12} \subset Mo^{VI}_{72}Fe^{III}_{30}] \cdot$ ca. 60 H_2O. The supramolecular MOB entity consists of two POM/MOB clusters [6, 7]:

- an oxidized icosahedral capsule as host, corresponding to the $[Mo^{VI}_{72}Fe^{III}_{30}]$ cluster (internal cavity diametre $\approx$ 16 Å);
- a Keggin molecule as nucleus or guest, corresponding to the reduced $[H_xPMo_{12}O_{40}]^{3-}$ (x=1-2) POM cluster (diametre $\approx$ 12 Å).

The novel pure POM/MOB supramolecular entity is presented in Fig. 3.

The noncovalent host-guest interaction indicates that the reduced Keggin cluster fits exactly into the capsule cavity. The shortest $O_{host}\ldots O_{guest}$ bond lengths of $\approx$ 2.6 Å are typical for hydrogen bonding. The new absorption band observed in visible at $\approx$ 550 nm, which contributes to the dark green colour of the compound, was temporarily assigned to a new electronic transition of the type reduced nucleus $\leftrightarrow$ oxidized capsule, but this assumption need to be confirmed [6].

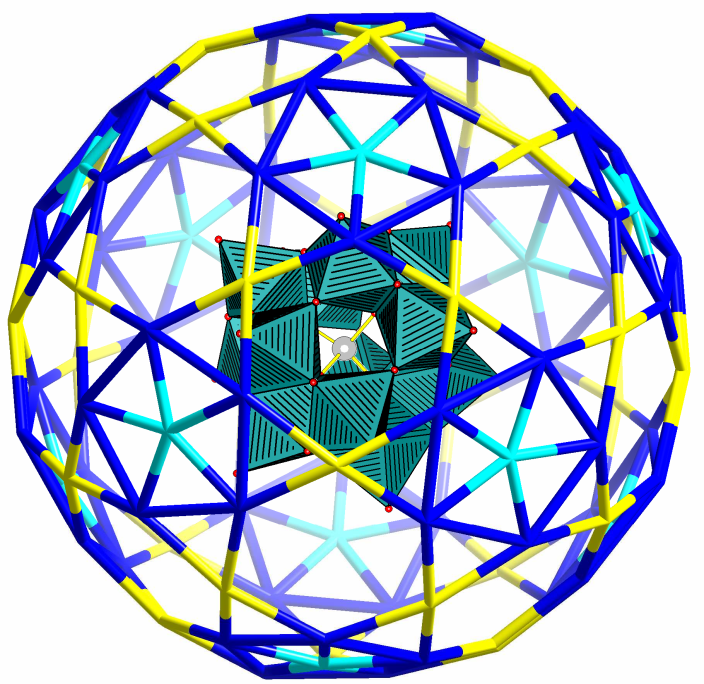


Fig. 3. Structure of the supramolecular $[PMo_{12} \subset Mo^{VI}{}_{72}Fe^{III}{}_{30}]$ entity. The $[Mo_{72}Fe_{30}]$ capsule (host) is figured in wire frame representation with the 30 Fe^{III} centres (highlighted as yellow wires) linking the 12 $[(Mo)Mo_5]$ pentagons (figured in blue and turquoise). The reduced $[PMo_{12}]$ nucleus (guest) is shown in polyhedral representation (with the P heteroatom as gray large sphere and the O atoms as small red spheres).

THROUGH POLYOXOMETALATE/METAL OXIDE-BASED CLUSTERS TOWARDS A NEW SUPER-SUPRAMOLECULAR CHEMISTRY?

The huge spherical POM/MOB clusters with giant sphere-type structure having overall icosahedral symmetry can also be formulated, according to a building block principle, as $(pentagon)_{12}(linker)_{30}$. The prototype is the very large $[Mo^{VI}{}_{72}Mo^{V}{}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]^{42-}$ POM cluster, abridged as $[Mo_{132}]$ or $[Mo^{VI}{}_{72}Mo^{V}{}_{60}]$ [8, 9]. Like all clusters with identical or similar structure, the pentagons are represented by 12 $[(Mo^{VI})Mo^{VI}{}_5O_{21}(H_2O)_6]^{6-}$ units, abridged as $[(Mo^{VI})Mo^{VI}{}_5]$. In the case of the $[Mo_{132}]$ cluster, 30 $[Mo^{V}{}_2O_4(CH_3COO)]^{+}$ units, abridged as $[Mo^{V}{}_2]$, act as linkers/spacers.

The 12 pentagonal units and the 30 linkers/spacers, out of which the $[Mo_{132}]$ giant sphere is built up, allow not only overall object sizing but also a sizing of the large number of tailor-made pores. The 20 $[Mo_9O_9]$ pores on the surface are rings with diametres between ≈ 0.6-0.8 nm.

The $[Mo_{132}]$ POM cluster with an external diametre of ≈ 2.9 nm has a large internal cavity having a diametre of ≈ 2.0 nm. The 20 pores are large enough to allow the passage of small spheres into the internal cavity. The fact that the $[Mo_{132}]$ POM cluster normally contains 100 encapsulated H_2O molecules was known. Interacting through the open pores with the crystal water, the assembly of 100 H_2O molecules has no special organization.

But late 2002 brought an unexpected surprise [10, 11]. If the 20 surface pores/rings, having receptor properties, are filled with organic ions, such as $[(NH_2)_3C]^+$ guanidinium cations, which fit exactly into the pores, the whole giant sphere surface becomes closed, see Fig. 4.

Closing the pores decreases the high negative charge of the cluster, stabilizes it and, especially, influences the structure of the encapsulated $[H_2O]_{100}$ system. Consequently, the 100 H_2O molecules are organized in a highly symmetrical spherical structure, in which 3 x 12 = 36 pentagons built up of H_2O molecules can be identified, see Fig. 5.

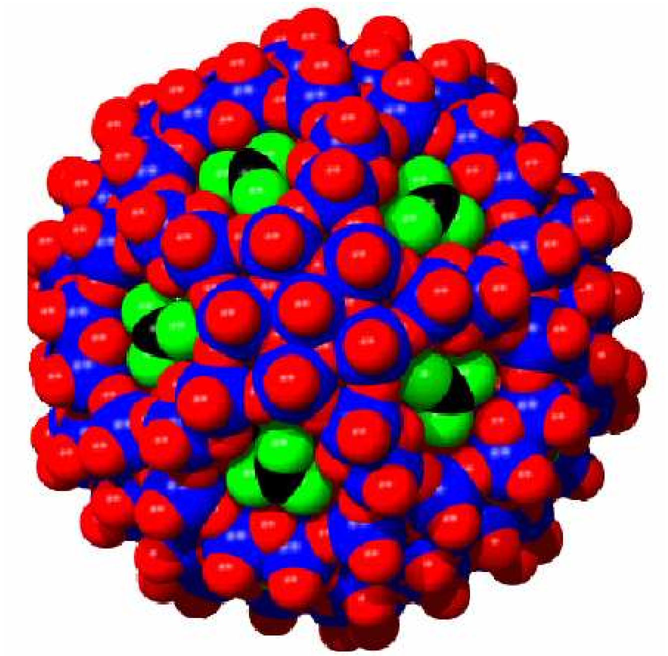


Fig. 4. Space filling representation of the $[Mo_{132}]$ POM cluster with the 20 pores closed with $[(NH_2)_3C]^+$ guanidinium cations. Color code: Mo=blue, O=red, C=black, N=green.

The amazing $[H_2O]_{100}$ aggregate/system consists of two Platonic solids, namely two dodecahedrons having each 20 pentagons as faces, and a very complex Archimedean solid, namely a rhombicosidodecahedron with 12 decagons, 20 hexagons and 30 tetragons as faces. Thus, the $[H_2O]_{100}$ system has in its centre a $[H_2O]_{20}$ dodecahedron, which is inside another larger $[H_2O]_{20}$ dodecahedron, surrounded in its turn by a $[H_2O]_{60}$ a rhombicosidodecahedron, see Fig. 6. The 100 H_2O molecules are thus linked that they form altogether a novel icosahedral cluster with tetrahedrally coordinated O atoms. (Each H_2O molecule is tetrahedrally surrounded by other four H_2O molecules.)

Such an auto-organization leading to structures never before met in chemistry is unprecedented. That is why, Müller considers that this could open the way towards a new super-supramolecular chemistry. He states that "we could now cross the frontier (of supramolecular chemistry) to a rather large multitude of receptor sites positioned on a stable nanoobject". While it became evident that a receptor-substrate supramolecule is characterized by its geometric, thermodynamic and kinetic features, new categories of receptor-substrate types appear in the present super-supramolecule and offer the chance to study a variety of relevant cooperative effects [10].

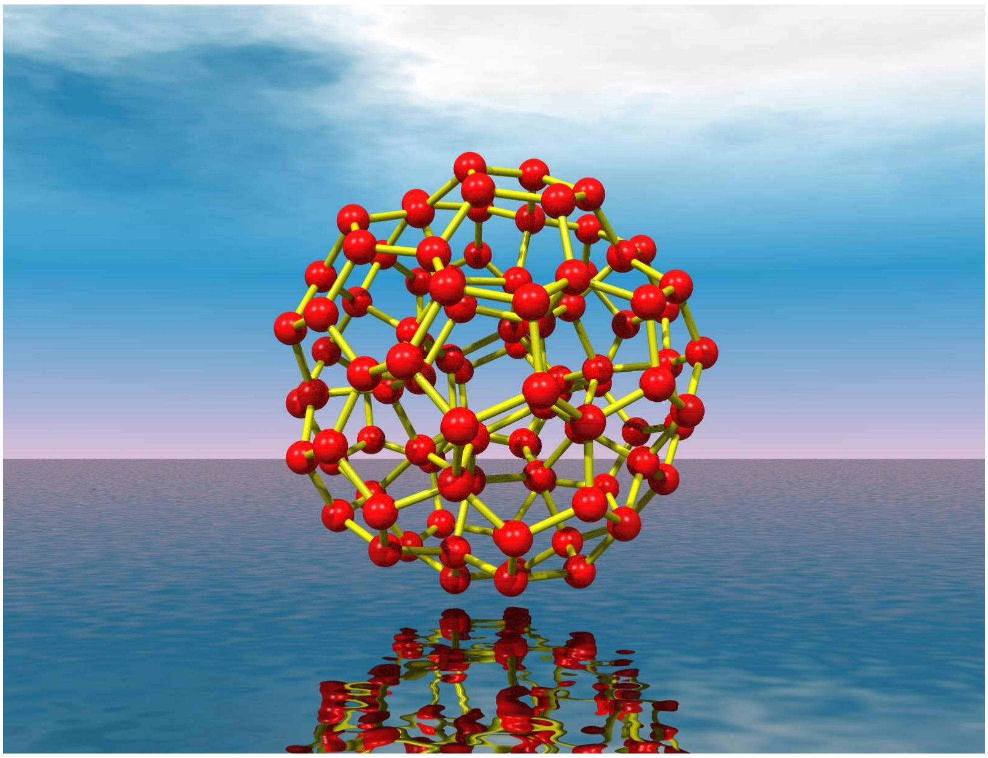
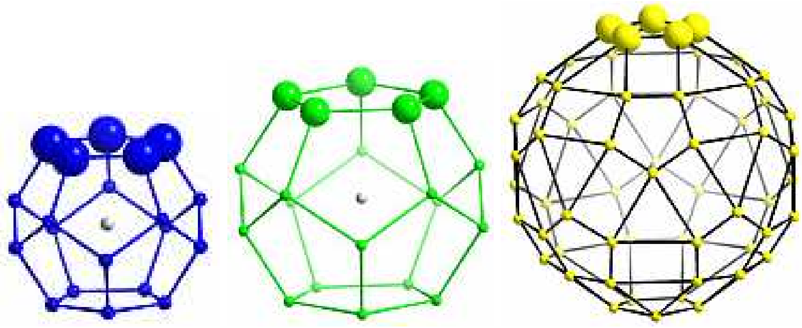


Fig. 5. Ball-and-stick representation of the organized $[H_2O]_{100}$ system (encapsulated in the $[Mo_{132}]$ POM cluster with closed pores).



$[H_2O]_{20}$ $[H_2O]_{20}$ $[H_2O]_{60}$

Fig. 6. Mixed wire frame and ball-and-stick representation of the first $[H_2O]_{20}$ dodecahedron (left), the second $[H_2O]_{20}$ dodecahedron (centre) and the $[H_2O]_{60}$ rhombicosidodecahedron (right), out of which the $[H_2O]_{100}$ system is built up.

Only the future will show whether Müller's suppositions were correct. The future will also reveal what other surprises are in store for us concerning these amazing substances which are the POM/MOB clusters.

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