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

I. GENERAL ASPECTS

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ABSTRACT. Current general aspects of the so-called polyoxometalate/ metal oxide-based clusters are reviewed.

Anionic molecules, for which the term polyoxometalate clusters is accurate and similar neutral molecules, for which the term metal oxide-based clusters should be used are discussed.

The justification for using the term cluster in the case of polyoxometalate/ metal oxide-based molecules, which contain only metal centres bonded exclusively through bridging oxygen atoms are presented.

Two generations of polyoxometalate/metal oxide-based clusters, named clusters of classic type, respectively clusters with supramolecular properties are also described and exemplified.

INTRODUCTION

Over the last ten years, the polyoxometalates have undergone a spectacular development surpassing even the most optimistic expectations of the relatively few research groups involved in investigations dedicated to this class of substances. The ceaseless diversification of polyoxometalates through the synthesis of an impressive number of new molecules having interesting electronic structures, high symmetry and unexpected topologies has broadened the frontiers of chemistry in a meso-physical world or nano-world, to be found somewhere between the micro- and the macroscopic realms [1].

All the above justifies, in our opinion, a review of certain current aspects of these amazing substances, in the wider context of the new tendencies and trends in chemistry.

The first part is dedicated to the presentation of several general aspects.

POLYOXOMETALATE/METAL OXIDE - BASED MOLECULES

According to a widely used definition, polyoxometalates (POMs) are the polyoxoanions of the early transition elements, especially Mo, W and V, constructed of linked MO_n units [2]. The M metal centres, which may belong to one or more atomic species, are named addenda.

Under the usual definition, POMs are exclusively anionic molecules (or molecular anions). The corresponding (electroneutral) compounds are in fact salts, usually hydrated, of the POM anions. For example, the yellow precipitate that is produced when ammonium molybdate is added to phosphoric acid, already described by Berzelius in 1826, correspond to the $(NH_4)_3[PMo_{12}O_{40}] \cdot$ $\cdot\, nH_2O$ compound. Its main constituent is the molecular unit, namely the $[PMo_{12}O_{40}]^{3-}$ anionic molecule, which in fact represents the POM proper. But between the POM molecular anion and the NH_4^+ external cations there are only electrostatic interactions (i.e. ionic bonds) and the crystal water is linked to the compound, more precisely to the external cations and to the molecular unit, only through noncovalent bonds (i.e. hydrogen bonds).

However, recently, the situation has undergone a change, especially through the reduction of a number of metal centres and/or the introduction of other metal centres having lower oxidation numbers than those usually associated with POMs. Thus, molecules having identical or similar structures with well-known POMs but which are however electroneutral and not anionic, were obtained. Consequently, POM clusters with giant sphere-type structures are well-known especially through their prototype, the $[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]^{42-}$ cluster, abridged as $[Mo_{132}]$ or $[Mo^{VI}_{72}Mo^{V}_{60}]$ [3]. But other molecules with similar structure containing only 102 metal centres were obtained, such as the $[H_4Mo^{VI}_{72}Fe^{III}_{30}O_{252}(CH_3COO)_{12}(H_2O)_{98}]$ cluster, abridged as $[Mo_{72}Fe_{30}]$ or $[Mo^{VI}_{72}Fe^{III}_{30}]$ [4], respectively the $[Mo^{VI/V}_{72}Mo^{V}_{30}O_{282}(CH_3COO)_{12}(H_2O)_{78}]$ cluster, abridged as $[Mo_{102}]$ or $[Mo^{VI/V}_{72}Mo^{V}_{30}]$ [5]. These cluster molecules are electroneutral. (It is to be mentioned that in the particular case of such electroneutral substances the terms compound and molecule are identical.)

It is obvious that for such neutral molecules the term POM with the ending -ate can no longer be used. They can be called simply metal oxide-based clusters, according to the term molybdenum-oxide based clusters used by Müller to designate the above mentioned molecules [4, 5].

We mention in passing that the term metal oxide-based (MOB) clusters is of a more general nature and can be applied to both electroneutral and electrically charged molecules (be they a anionic or, why not, even cationic). On the other hand, the traditional term POM clusters is valid only in the case of anionic molecules.

Possibly a hybrid term, such as polyoxometalate/metal oxide-based clusters, POM/MOB clusters for short, would be appropriate for covering completely the range of these remarkable molecules.

CLUSTERS WITHOUT DIRECT METAL-METAL BONDS

Initially the term (metal) cluster was used to designate coordination compounds which, instead of the central atom, contain a polyhedron made up of metal atoms linked by metal-metal bonds, forming a sort of cage surrounded by ligands. Later on, the term cluster was extended to cover the compounds/ molecules (the distinction compound-molecule is ignored again) also containing in the polyhedron non-metal atoms and having certain bridged by ligands (and not direct) metal-metal bonds. Currently, the term cluster is used for polymetallic compounds/molecules with direct metal-metal bond(s).

But, in the last few years, POM/MOB molecules are more and more frequently called clusters, although the bonds between metal centres are exclusively bridged by oxygen atoms. This could also be a consequence of the frequent use of the abridged formula of POM/MOB molecules, involving only heavy atoms (more precisely, the species acting as central atoms in a certain group of the molecule) which often are identical with the metal centres, e.g. $[Mo_{132}]$, $[Mo_{154}]$, $[Mo_{176}]$, $[Mo_{368}]$ etc.

Certain authors working directly in the POM field are in favour in this tendency, which extends the term cluster to cover all compounds/molecules having several metal centres, without going into any distinction as to the nature of the metal-metal bonds [6]. Other authors, especially those who have made their mark in other fields than POMs, question such an extrapolation and affirm that POMs and similar substances should be considered only cage compounds [7]. In fact, it is all a matter of option and preference.

Working in the POM chemistry, we will use the general term POM/ MOB clusters, also allowing the avoidance of the trap represented by the terms compound and molecule, frequent in the case of these substances.

TWO GENERATIONS OF POLYOXOMETALATE / /METAL OXIDE-BASED MOLECULES

As mentioned above, in the past ten years the chemistry of POM/MOB clusters brought about spectacular changes, due to the synthesis and characterization of giant molecules with new structures having high symmetry and remarkable topological and electronic properties. Consequently, we can talk about two distinct generation of POM/MOB clusters: one of classical type and another with supramolecular properties.

The classical POMs, which are exclusively anionic molecules, have the characteristics and properties of the traditional coordination compounds, more exactly of the molecules which form the so-called complex. They are obtained through simple intermolecular condensation of certain oxoanions that generates polyoxoanionic buildings. Depending on the nature of the oxoanion(s) involved in the condensation process and the pH value, a large number of POMs with various structures and properties were obtained. In an exaggeratedly simplified classification, polyoxometalates (POMs) are divided in isopolyoxometalates (IPOMs) and heteropolyoxometalates (HPOMs), while in the condensation process are involved oxoanions from one or several atomic species. Rigorously speaking, in the case of IPOMs are present exclusively one of more atomic species with addenda role, while in the case of HPOMs are also present one or more atomic species with heteroatom role. The positions of the addenda and the heteroatom(s) are well defined for every structure.

20-30 years ago, the chemistry of IPOMs had become a closed area, with very limited perspectives of future development. The maximal number of metal centres seems to be limited to 10-12 atoms. On the other hand, the HPOM chemistry field knew a constant if not spectacular development. The presence of another atomic species having heteroatom role, which can be selected from about 70 elements of the periodic table, gives to the POMs not only more stability, a larger variety or the possibility of increasing the number of metal centres, but also new properties which allow for new applications. Practically, until quite recently, the POM chemistry was concentrated almost exclusively on the synthesis and investigation of new HPOMs, to which are added the research of new application.

Our chosen example of classical POM is a cluster synthesized and characterized by us, with the formula $[H_3Sb^{III}V^{IV}W_{17}O_{60}]^{8-}$, not published until now [8]. The corresponding neutral compound is $Na_2(NH_4)_6[H_3Sb^{III}V^{IV}W_{17}O_{60}] \cdot 16H_2O$.

Single-crystal X-ray diffraction analysis shows that the anionic HPOM molecule is made up of two halves, each of trilacunary Keggin-type, i.e. $[SbM_9O_{33}]$ and $[M_9O_{33}]$, linked by corners and edges and sharing six O atoms, see Fig. 1. Practically, the Sb^{III} heteroatom is statistically distributed between the two halves. The Sb^{III} heteroatom is tricoordinated building a trigonal SbO_3 pyramid in the $[SbM_9O_{33}]$ unit. The unshared pair of electrons of Sb^{III} which has a nonbonding character is pointed towards the other half-anion.

The 17 W atoms and the V^{IV} atom, which belong to the two atomic species having an addenda role, can occupy any of the 18 addenda position noted with M (M=W, V). Practically, all the 18 addenda atoms are delocalized and cannot be differentiated. (We dislike to consider and to call the V^{IV} centre, which occupy an addenda position, as secondary heteroatom.)

It should also be mentioned the fact that every M addendum/metal centre is located in the centre of a distorted MO_6 octahedron. The addenda occupy off-centre position towards the external edges, due to certain π $M \rightarrow O$ $(d\pi\text{-}p\pi)$ bonds, which reinforce the coordinative covalent $M \leftarrow O$ bonds. Each M metal centre has only one terminal O atom.

All the bonds figured in the ORTEP diagram are covalent, namely the bonds between addenda/metal centres and oxygen atoms, respectively between the heteroatom and oxygen atoms, i.e. M-O and X-O. As can be noticed, the addenda/metal centres are linked between each other and with the heteroatom exclusively by oxygen bridged covalent bonds.

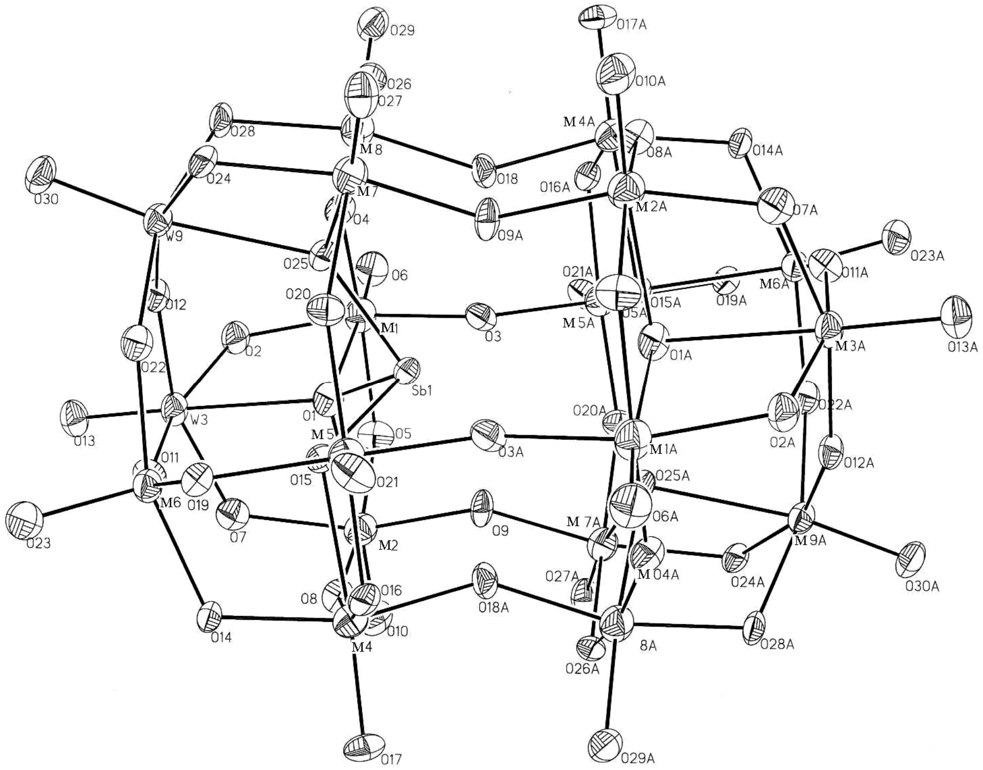

Fig. 1. ORTEP diagram of the $[H_3Sb^{III}V^{IV}W_{17}O_{60}]^{8-}$ HPOM cluster (M=W, V).

Investigations on POM clusters with the general formula $[H_nXM_{18}O_{60}]^{p-}$ have revealed that the nH atoms are non-ionizable and belong to the anionic building. Evidently, the small H atoms cannot be identified by single-crystal X-ray diffraction analysis. Given that Keggin-type and Keggin-derived structures with central lacunae (in the place reserved for the heteroatom) are not known, Krebs and Klein consider that the non-ionizable H atoms are to be found inside the O_3 cavity [9]. The nature of the bonds in the unusual H_3O_3 group is not known, but it is probably the case of weak multicentre covalent bonds.

The $[H_3Sb^{III}V^{IV}W_{17}O_{60}]^{8-}$ HPOM anion has a C_3 symmetry axes and an orthogonal symmetry plane. Because it shows similarities but also differences compared to the well-known Dawson structure of the HPOMs with the formula $[X_2M_{18}O_{62}]^{q-}$, Krebs and Klein proposed the term non-Dawson for the HPOMs with a structure similar to the one studied by us, having the general formula $[H_nXM_{18}O_{60}]^{p-}$. As we have serious reservation concerning the use of the prefix non- in denominations, we prefer to name this structure pseudo-Dawson.

The new generation of POM/MOB clusters appeared only around ten years ago, but its representatives became instantly well-known worldwide and their reputation has gone beyond the realm of chemistry, mainly as a result of the Bielefeld University research team led by Achim Müller.

The new generation of very large POM/MOB molecules is based upon a novel synthesis strategy that allows, on the basis of a number of simple combinatory linkable building blocks/units at disposition, the obtaining by successive and rapid processes of self-assembly, self-organization and molecular growth of a large variety of huge molecules. The basic chemical principles for the synthesis of the new giant molecular species are: the existence of a library of linkable building blocks/units, the presence of reducing agents in the system to reduce a number of metal centres, the introduction of heteroatoms with different oxidation numbers, the introduction and/or exchange of various ligands other than oxygen (the oxide ion), which offer the possibility to tune the electron density etc. [10-13].

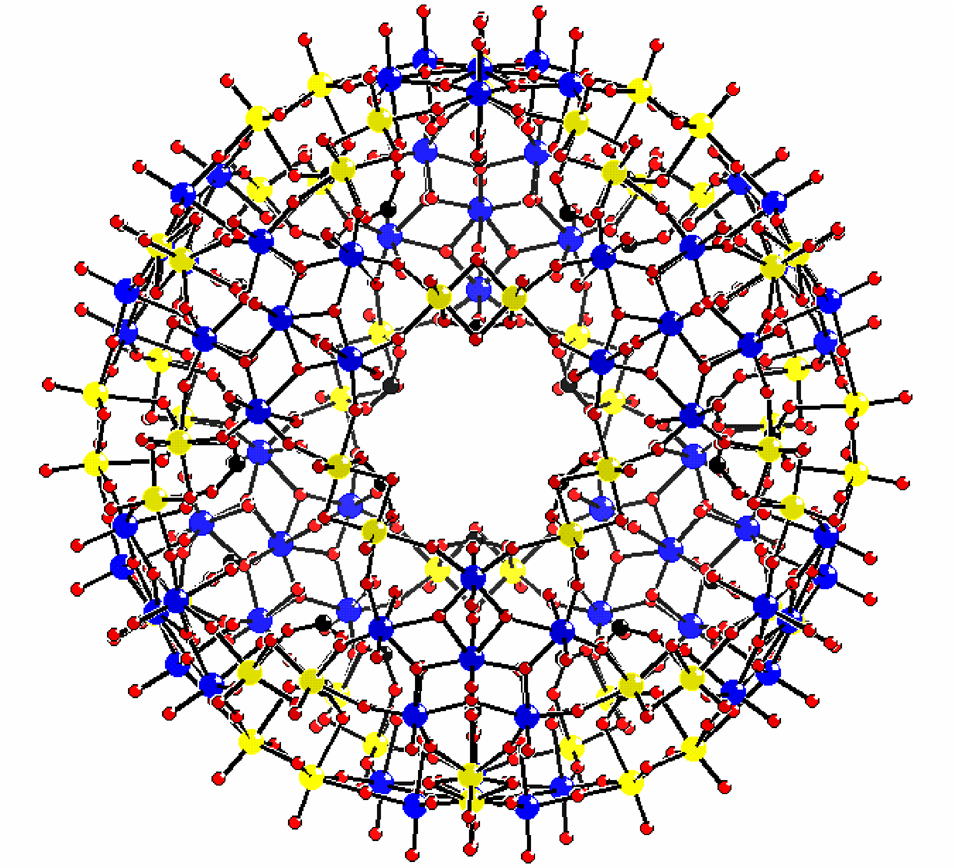

Fig. 2. The $[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]^{42-} \equiv [Mo_{132}]$ POM cluster in ball-and-stick representation. Color code: Mo^{VI} blue, Mo^{V} yellow, C black, O red.

In the case of classical POM/MOB clusters, the most interesting structures belong to the HPOMs with W as addendum. Somewhat surprisingly, the new generation of POM/MOB clusters developed inside or within the IPOMs with Mo as addendum. This is due mainly to the fact that Mo can offer a much larger variety of linkable building blocks and the reduction of certain Mo^{VI} to Mo^{V} metal centres occurs more easily than in the case of W. However, for the new generation of POM/MOB clusters the distinction iso-/hetero- is surpassed. The specific positions of the (metal) centres are those of addendum and linker/spacer, which are localized in the centre of building blocks/units and linker/spacer units.

The mixed valence $[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]^{42-}$ POM cluster, abridged as $[Mo_{132}]$ or $[Mo^{VI}_{72}Mo^{V}_{60}]$, obtained in 1999 by Müller and his team, is probable the most aesthetically molecule synthesized so far [3]. The spherical $[Mo_{132}]$ POM cluster is constructed of 12 $[Mo^{VI/V}_{11}]$ building blocks, which can also be decomposed in 12 $[(Mo^{VI})Mo^{VI}_5O_{21}(H_2O)_6]^{6-} \equiv [(Mo^{VI})Mo^{VI}_5]$ and 30 $[Mo^{V}_2O_4(CH_3COO)]^{+} \equiv [Mo^{V}_2]$ units, the latter with linker/spacer role.

The so-called "giant sphere" structure of the $[Mo_{132}]$ cluster having an overall icosahedral symmetry is presented in Fig. 2.

All the bonds between the atoms of the $[Mo_{132}]$ POM cluster are covalent. These demonstrate that the term "the new generation of very large supramolecular POM clusters" we used in a previous review could be considered exaggerated [14]. If in the case of molecules, the mandatory characteristic is the existence of covalent bonds between the constituent atoms, to which possibly other bonds can be added, supramolecules are characterized by the mandatory presence of noncovalent bonds and by certain special properties. These special properties (the presence of a few is sufficient) are: multicomponent nature, cooperative action of the components, self-assembly and even self-organization, host-guest interactions etc.

A first observation is that usually the supramolecule is not also a discrete molecule, but rather an assembly/entity of discrete molecules linked by noncovalent bonds. Initially Lehn, one of the fathers of supramolecular chemistry, considered that the unusual properties of supramolecules, which open up new avenues in chemistry, are mainly due to the existence of noncovalent bonds. He even defined supramolecular chemistry as "the chemistry of noncovalent bonds" [15].

Perhaps it would have been better to define supramolecules exclusively by their characteristic properties, that truly bring something new to chemistry, and not through the existence of certain types of bonds. And that because it was consequently demonstrated that there exist substances, and we mean especially the POM/MOB clusters, having the properties of supramolecules but lacking noncovalent bonds. And not only that but the largest synthesized and structurally characterized molecules, which contain up to 368 metal centres, belong to these very clusters.

As a consequence, we appreciate that the new generation of the molecules under discussion could be named POM/MOB clusters with supramolecular properties or pseudosupramolecular POM/MOB clusters.

The second part of the review will be dedicated to the presentation of certain special aspects of these clusters with supramolecular properties.

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