The Nomenclature of Polyoxometalates: How To Connect a Name and a Structure[†]

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I. Introduction: What Is Nomenclature?

At first glance, nomenclature may seem of secondary importance. Actually it is a means to com-

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municate and to exchange information as accurate, as precise, and as detailed as possible.

To this respect nomenclature may be called a language. There are words or nouns, i.e., the names of the elements, and there is a grammar, i.e., a method of assembling them. The aim is to carry a maximum of information with a minimum of stems, prefixes, suffixes, numbers, and/or letters used as locants, etc., each of them having a specific meaning. The idea is to cast a "name". A "name" is before anything a code to refer to a given compound. In the beginning, names were trivial. It was the way alchemists referred to compounds. It was the way chemists first referred to compounds. They, chemists and compounds, were only a very few. Everybody understood what was meant, everybody understood what was vitriol. One just had to be a member of the "club" to understand this kind of slang. However as soon as the number of chemicals exploded, the system became untractable. Something else was needed. This was the origin of the treatise of nomenclature of Lavoisier and Guyton de Morveau, and the birth of nomenclature.

Nevertheless, even today, trivial names continue to be used in many cases because they are short and convenient. A nomenclature system always reflects

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[†] The following conventions have been adopted for the presentation of nomenclature and formulae in this review. A name may be either shorter or longer than the line. If it is longer, the break in the name has been chosen, if possible, just after an hyphen which then finishes the line. If this was not possible the sign = has been used to finish the line. This convention means that if the lines were extended, those ending with a hyphen would retain the hyphen and those ending with the = would be joined without any further punctuation.

the state of the art at the time it is launched. It needs agreement and then long discussions between chemists. Quite often, the imagination and the skillfulness of chemists run much faster than nomenclature proposals. Surprises are still occurring in chemistry. To name unexpected compounds, chemists are inventing new trivial names exciting our imagination because the known nomenclature system does not provide easy solutions if any. A recent example is given by fullerenes. Who could understand at its base what such a name means, except for maybe some architects, who are, by the way, not so much interested in chemistry except in its applications. Another origin of trivial names resulted in the past from the discovery of new compounds at a time analytical chemistry was the only tool to identify a compound, and trivial names still survive today. Such is the case of polyoxometalate chemistry with names such as paratungstate or Preyssler compound. Structures were not known and it was not possible to determine them. But with the use of X-ray diffraction, structures were so unusual at the time they were determined that the name of the crystallographer was used: examples are Keggin compound and Lindqvist compound. Those names are commonly used and will be a long time due to their convenience.

Trivial names were and are understood only by those working in the field. They say nothing about the composition; they say nothing about the structure. For example, paratungstate-A and paratungstate-B are completely different structurally speaking; their common feature is that they are both polyoxometalates. But experts know what they are talking about; mentioning such a trivial name means something for them because they immediately establish a connection among the trivial name, the formula, and the structure.

Chemists need names to discuss about their work and for retrieval purposes. Today the idea is that a systematic name must carry full information about the composition and the structure which must be rebuilt from the name. Depending on the level of exchange of information, the complexity of a name will follow the degree of sophistication to be incorporated into the name. In organic chemistry, the tetravalence of carbon is such a strong and general feature that reflecting bonds in nomenclature is enough to describe a structure. This implies a substitutive system of nomenclature starting from a parent compound. In inorganic chemistry, chemical bonds tend to be more complicated, more subtle; it is more difficult to describe bonds as single, double, triple, etc. Another system is used. Structural features are incorporated into the name with the use of an additive principle which is the base of coordination compound nomenclature. Ligand names are added to this of the central atom.

Polyoxometalates are treated this way but they exhibit a special feature, the high number of central atoms. The most common metal surrounding is octahedral. Some other environments are characterized by a tetrahedron, or a square pyramid, or more seldomly a pentagonal bipyramid. Tetrahedron is constantly treated as a ligand. Moreover those polyhedrons are fused, having common vertices and common edges, even sometimes common faces. The various sharings may also occur in the same compound, thus increasing the difficulty.

Thus the central part of the problem is to name the core of fused octahedrons or, to be more precise, how to refer to each metal atom of the fused core and to each position of its polyhedral surrounding. Rules have been published by the Commission of Nomenclature of the International Union of Pure and Applied Chemistry.[1] They are reviewed in the first part of this review. They will then be applied to polyoxometalates arbitrarily divided into two categories, isopolyoxometalates (or homopolyoxometalates) and heteropolyoxometalates. The second category is mainly based upon the Keggin structure which is most of the time a main group element tetrahedron around which is wrapped an assembly of fused octahedrons.

II. A Review of IUPAC Recommendations

II.1. Coordination Compounds: Abridged Rules

Full details are found in Nomenclature of Inorganic Chemistry issued by the Commission of Nomenclature of Inorganic Chemistry of IUPAC.[2]

(a) Every formula should be enclosed in square brackets. Metal atoms should be cited first, in alphabetical order if several species occur. Formally anionic ligands are cited next in alphabetical order according to the first symbol of their formula. Neutral ligands follow in alphabetical order according to the first symbol of their formula. Some applications require flexibility in the writing of formulae. For instance other sequences may be used in the case special structural features are to be shown.

(b) In names, ligands are cited in alphabetical order, without regard to the charge, before the names of central atoms. Numerical prefixes indicating the number of ligands are not considered in determining that order. The overall charge is indicated between parentheses at the end of the name.

Numerical prefixes are derived from cardinal numerals, di-, tri-, etc; enclosing marks are not required. The prefixes bis-, tris-, etc. are used in complex expressions and when required to avoid ambiguity; enclosing marks are placed around the multiplicand. Used prefixes are listed in Table 1.

(c) The nesting of enclosing marks for names is ( ), [( )], {[( )]}, {{[( )]}}, etc.

(d) Bridging ligands are indicated by the Greek letter μ appearing before the ligand name and separated by an hyphen.

The whole term is separated of the rest of the name with a hyphen, or with parentheses if more complex situations arise. Multiplicative prefixes may be used if the bridging ligand occurs more than once; the prefixe is placed before μ and separated by a hyphen, e.g. tri-μ-oxo.

The bridging index, i.e., the number of coordination centers connected to one bridging ligand, is indicated by a right subscript μ_n, where $n \geq 2$; this is valid regardless of the bridge's length or orientation, a single atom or a molecule or an ion ligated to several centers by different atoms. Bridging ligands are cited

Table 1. Multiplication Prefixes[a]

1	mono	20	icosa
2	di	21	henicosa
3	tri	22	docosa
4	tetra	23	tricosa
5	penta	24	tetracosa
6	hexa	30	triaconta
7	hepta	31	hentriaconta
8	octa	32	dotriaconta
9	nona	33	tritriaconta
10	deca	34	tetratriaconta
11	undeca	40	tetraconta
12	dodeca	50	pentaconta
13	trideca	60	hexaconta
14	tetradeca	70	heptaconta
15	pentadeca	80	octaconta
16	hexadeca	90	nonaconta
17	heptadeca	100	hecta
18	octadeca	132	dotriacontahecta
19	nonadeca		

[a] Other multiplicative prefixes are bis, tris, tetrakis, pentakis, hexakis, heptakis, octakis, nonakis, decakis, etc. They are used together with the cardinal prefixes when ambiguity may arise, e.g. bis(tetraoxomolybdate).

in alphabetical order along with other ligands, but a bridging ligand is cited before the nonbridging ligand, e.g. μ-oxo-trioxo. Multiple bridging is listed in descending values of n.

(e) The number of central atoms is indicated by a numerical prefix. For anionic species, the suffix −ate is added after the central atom list; when there is only one atomic species, −ate is attached to the stem of the element name, e.g. tungstate; when there are several chemical species, their element names are listed in alphabetical order with convenient mutiplicative prefixes, whatever numbering locants are, enclosed in parentheses with the suffix −ate after the parenthesis without hyphen.

II.2. Numbering of Condensed Polyoxometalates

The numbering of a condensed structure is based on the unsubstituted parent structure for the polyanion taken with an idealized symmetry. The central atoms of the octahedral units are numbered and the ligand positions are indicated by a secondary set of letter locants. Tetrahedral units are treated as bridging ligands.

Polyhedrons constructed from octahedrons contain rotational symmetry axes and skeletal planes. Such planes are defined as those planes (or quasiplanes) containing several octahedral centers.

The following numbering rules are applied sequentially.

1. Choice of Reference Axis (Figure 1).

(a) The reference axis is the rotational axis of the idealized polyanion structure of highest order; it is oriented vertically.

(b) Perpendicular to the reference axis, several skeletal planes may be encountered. The skeletal plane which lies farthest from the centroid of the polyanion is described as a terminal skeletal plane; others, as internal skeletal planes.

(c) When there are more than one symmetry axes of highest order, the preferred axis is that one which is perpendicular to the greatest number of skeletal planes.
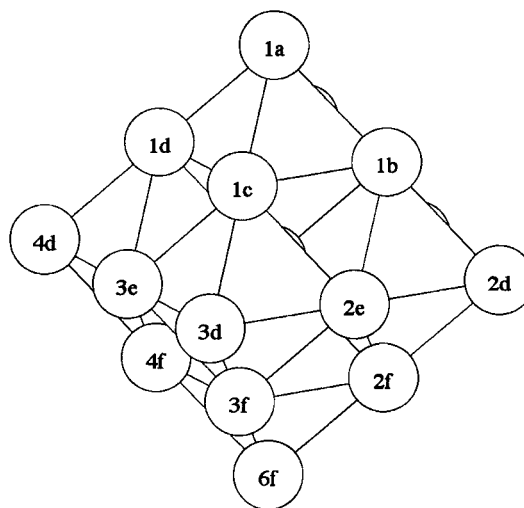

Figure 1. Six fused octahedrons, as found in $[Nb_6O_{19}]^{8-}$, with the locant assignment of some octahedron vertices. The reference axis goes through oxygen atoms 1a and 6f. The reference plane goes through atoms 1a, 3e, and 6f.

(d) When the polyanion has no axis of symmetry, the reference axis then is the axis perpendicular to the skeletal plane with the greatest number of octahedral centers.

2. Choice of Terminal Skeletal Plane.

(a) The preferred terminal skeletal plane is that plane with the fewest number of central atoms. The reference axis is then oriented in such a way that the preferred terminal plane is the uppermost plane.

(b) When both terminal planes contain the same number of central atoms, the preferred plane is that plane with the least condensed fusion of octahedrons (i.e., when the number of bridges between central atoms is the lowest; vertex sharing is less condensed than edge sharing which is less condensed than face sharing).

(c) See 4.

(d) When a further choice is necessary, the preceding rules are applied considering the first internal skeletal plane, and so on.

3. Choice of Reference Symmetry Plane.

(a) The reference plane is defined as the symmetry plane which contains the reference axis and which also contains the lowest number of central atoms.

(b) When there is more than one reference symmetry plane which satisfies this requirement, then the preferred plane is that one which contains the most atoms in common with the preferred terminal skeletal plane.

(c) The reference symmetry plane is divided by the reference axis in two halves which must be designated. A 6 o'clock−12 o'clock line is defined by the intersection of the reference symmetry plane and a skeletal plane; thus it is perpendicular to the reference axis and the 12 o'clock position is in the half of the reference plane which contains the largest number of central atoms; 6 o'clock designates the other half.

(d) See 4 and 5.

(e) When a choice is left, the 12 o'clock position is on a ligating atom.

Table 2

He	Li	Be												B	C	N	O	F
Ne	Na	Mg												Al	Si	P	S	Cl
Ar	K	Ca	Sc		Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
Kr	Rb	Sr	Y		Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
Xe	Cs	Ba	La → Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
Rn	Fr	Ra	Ac → Lr															

4. Numbering of Central Atoms.

(a) Central atoms are numbered starting from the 12 o'clock position in the preferred terminal skeletal plane and turning clockwise (or counterclockwise). When a skeletal plane is fully numbered, the next skeletal plane located immediately below is numbered; the first atom to be numbered is the one which is met starting from the 12 o'clock position, turning clockwise or counterclockwise, depending on the lowest locant requirement (see 4 and 5).

(b) When a central atom or a ligand is substituted (see 5), it does not lower the symmetry of the skeleton for the choice of the reference axis and for the choice of the reference symmetry plane. However, locants are chosen in such a way that a central atom or a ligating atom appearing first in Table 2 has the smallest possible number or the earliest possible letter. When the polyanion contains several central atoms of several atomic species, the largest number of atoms of the species coming first in Table 2 will be numbered before numbering an atom coming second in Table 2, and so on.

(c) When several centers are occupied by the same atomic species under various oxidation states, the lowest oxidation state is given the lowest possible locant.

5. Octahedron Vertex Designation.

(a) In each octahedron letter locants are assigned to vertices as follows: define a line going through the central atom of the considered octahedron and parallel to the reference axis. This is the local reference axis. These two axes make a new reference plane valid for this octahedron only. The vertices of the octahedron are in local skeleton planes perpendicular to these two axes. In each local skeletal plane, the local 6 o'clock−12 o'clock line is the line intersecting the local reference axis and the mean reference axis. The intersection with the main axis is the 12 o'clock position in the considered local skeletal plane.

Letters, a−f, are assigned starting from the upper local skeletal plane. The (possibly several) vertices in a given local skeletal plane are assigned letters turning clockwise around the local axis, starting from the local 12 o'clock position.

If the local and the main axis coincide, then the local reference plane is the polyanion reference plane. The same set of rules is applied sequentially to give a letter locant designator to each vertex.

(b) If a choice exists in assigning letter locants to vertices, vertices are ordered according to the position in Table 2 of the ligand atom occupying them. An earlier position in Table 2 is assigned a letter coming earlier in the alphabet. In this connection, monoatomic ligands precede polyatomic ligands with the same ligating atom, e.g., oxygen atoms of OH or $CH_3=$ COO are considered to come immediately after oxygen and before any other element.

III. Isopolyanions

Traditionally, isopolyanions are polyanions containing only transition metals. Main group elements may appear but they are considered as ligands only, not as a part of the framework.

Many isopolyanions are known today and the number of published structures increases rapidly with synthesis in nonaqueous solvents and with the use of ligands other than oxo ligands. Isopolyanions may be based upon various metallic frameworks with a number of metal centers varying from 2 up to over 150. Involved metals are vanadium, niobium, tantalum, molybdenum, tungsten, and more seldomly some others. There are mixed species involving several types of metal atoms. It is also possible to have polyoxometalates in which other ligands having incorporated, for instance thio, or nitrosyl, or various organic moieties, all of them replacing oxo ligand(s) of a parent structure. Finally mixed species in which the same metal species occurs under various oxidation states are known.

III.1. The Lindqvist Structure

The most well known and the most symmetrical structure of isopolyanions results from the fusion of six octahedrons sharing a common vertex; an oxygen atom is bound to six metal centers. In coordination nomenclature this oxygen is referred as μ_6.

Lindqvist studied the structure of $Na_7H[Nb_6O_{19}]$·= $16H_2O$.[3] By concentrating on the name of the polyanion $[Nb_6O_{19}]^{8-}$, it is sufficient to count oxygen

atoms of various kinds, i.e., terminal and bridging oxygen atoms, either μ_2 and μ_6 (Figure 1):

μ_6-oxo-dodeca-μ-oxo-hexaoxohexaniobate(8−)

A multiplicative prefix may be used to shorten the name and to indicate that each niobium is bound to a terminal oxygen atom:

μ_6-oxo-dodeca-μ-oxo-hexa(oxoniobate)(8−)

The use of hyphens and the sequence of μ_6-oxo and μ-oxo strictly follow coordination nomenclature rules.

Shortening the name to hexaniobate would make it much simpler but it is ambiguous because it says nothing about the structure and the geometry of the polyanion, that is about the assembly of polyhedrons. The name nonadecaoxohexaniobate would only ring a bell for experts. This is why all the oxygen atoms with their structural feature, μ_6-oxo and μ-oxo, are designated.

The same principles may be applied without any difficulties to isopolyanions having the same structure, for example, $[Ta_6O_{19}]^{8-}$, $[Mo_6O_{19}]^{2-}$, and $[W_6O_{19}]^{2-}$.

III.2. Reduced Compounds

Isopolyanions may be reduced. The electron(s) appears to be delocalized over the metal framework and the structure is not changed. Thus it is straightforward to name the polyanion similarly by just changing the ionic charge. $[Mo_6O_{19}]^{2-}$ reduced by one electron is $[Mo_6O_{19}]^{3-}$:

μ_6-oxo-dodeca-μ-oxo-hexa(oxomolybdate)(3−)

III.3. Isopolyanions with Five Metal Centers

A family of polyanions containing five metal centers has been found: $[Mo_5O_{15}(PO_4)_2]^{6-}$,[4] $[W_5O_{15}(PO_4)_2]^{6-}$, $[Mo_5O_{15}(HPO_4)_2]^{4-}$, and $[Mo_5O_{15}(SO_3)_2]^{4-}$. The metal skeleton forms a ring (Figure 2). It is made of five octahedrons assembled in such a way that octahedrons 1 and 2, 2 and 3, 3 and 4, 4 and 5 share an edge while 1 and 5 share only one corner. This five-octahedron ring is capped on each side by a tetrahedron the basal three oxygen atoms of which
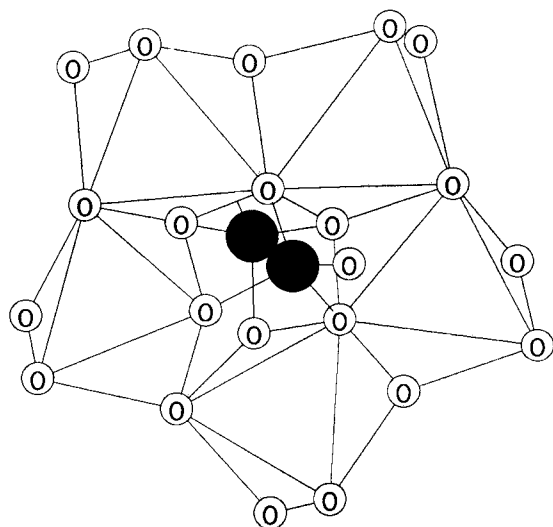
are shared with the five octahedrons. These tetrahedrons are treated as ligands. The name does not raise any particular difficulty:

di-μ_5-(tetraoxophosphato-O,O',O'')-penta-μ-oxo-pentakis(dioxomolybdate)(6−)

The use of pentakis is made necessary in order to avoid ambiguity with dioxomolybdate. Of course this part of the name might be as well ...decaoxopentamolybdate.

The number of central atoms, type of bridges, and the charge allows the structure to be built from the name, which is the goal of nomenclature.

A somewhat similar compound occurs with $C_6H_5=SO_2^-$ which now is bridging four molybdenum atoms instead of five in $[Mo_5O_{15}(C_6H_5SO_2)_2]^{2-}$:[4]

penta-μ-oxo-bis-μ_4-[dioxophenylsulfato(1−)]-pentakis(dioxomolybdate(2−)

III.4. Isopolyanions with a Larger Number of Metal Centers

Other polyanions may be named by following the same procedure. For example the name of $[Mo_7O_{24}]^{6-}$ is[5]

di-μ_4-oxo-di-μ_3-oxo-octa-μ-oxo-dodecaoxohepta=molybdate(6−)

The octamolybdate known as β-$[Mo_8O_{26}]^{4-}$ is named as (Figure 3)[6]

di-μ_4-oxo-tetra-μ_3-oxo-hexa-μ-oxo-tetradecaoxo=octamolybdate)(4−)

The α-octamolybdate which has a completely different structure will be discussed later on, and it will be seen that the name allows a clear distinction.

The case of dodecatungstates is interesting because there are two dodecatungstates: one is known as the paratungstate-B with the formula $[W_{12}O_{40}(OH)_2]^{10-}$ (Figure 4)[7] while the other derives from the Keggin structure (vide infra) with the formula $[W_{12}O_{38}(OH)_2]^{6-}$.

They are already distinguished by their number of oxygen atoms. They might be named as acidic anions:

dihydrogendotetracontaoxododecatungstate(10−)

or

dihydrogentetracontaoxododecatungstate(6−)

A more complete name may be built, which reflects the various types of oxygen bridges and the location of the hydrogen atoms. Of course such names are
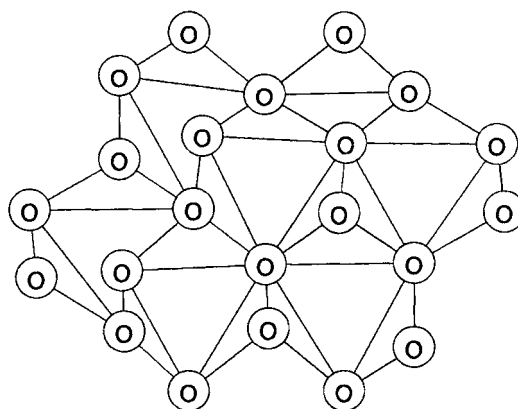

Figure 2. $[Mo_5O_{15}(PO_4)_2]^{6-}$, a five octahedron polytungstate capped on both sides by two phosphate tetrahedrons. Oxygen atoms are shown by O inside a circle; phosphorus atoms are shown as black circles.

Figure 3. The isopolyanion $[Mo_8O_{26}]^{4-}$ trivially called β-$[Mo_8O_{26}]^{4-}$. Oxygen atoms are shown by O inside a circle.

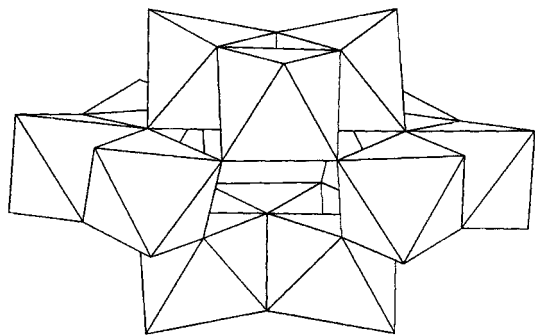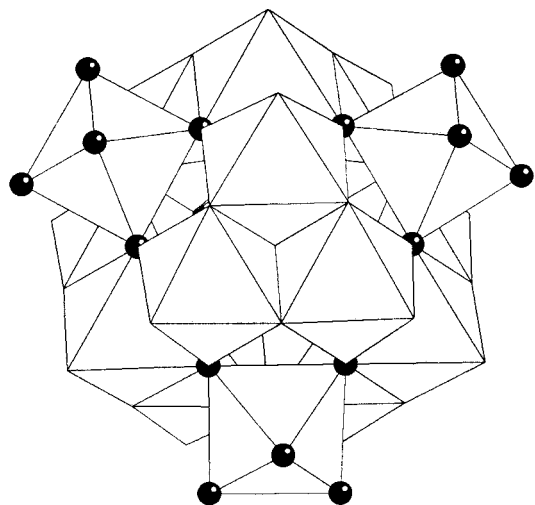**Figure 4.** $[W_{12}O_{40}(OH)_2]^{10-}$ trivially known as paratungstate-B.

Figure 5. The isopolyanion $[H_2Mo_{16}O_{40}(OH)_{12}]^{6-}$. The anti-Lipscomb molybdenum octahedrons are shown with oxygen atoms at vertices as black circles.

becoming more complicated but they allow the whole structure to be rebuilt:

di-μ_3-hydroxo-tetra-μ_3-oxo-octadeca-μ-oxo-octadecaoxododecatungstate(10−)

or

di-μ_3-hydroxo-di-μ_3-oxo-tetracosa-μ-oxo-dodecakis(oxotungstate)(6−)

Another example is $[H_2Mo_{16}O_{40}(OH)_{12}]^{6-}$. This compound derives from the Keggin structure (vide infra) in which the four Mo_3O_{13} groups have been turned by 60° (Figure 5). Above each of the four intersections is located a MoO_3 group making another octahedron by sharing three oxygen atoms with the preceding twelve metal center framework. This polyanion contains molybdenum(V) and molybdenum(VI).[8] They are treated as two different metal centers which are cited in the increasing order of oxidation states. The name is

hexadeca-μ_3-oxo-dodeca-μ-hydroxo-{dodecakis=[oxomolybdenum(V)]tetrakis[trioxo=molybdenum(VI)]}ate(8−)

III.5. Vanadium Compounds

Vanadium has a very rich and very complicated chemistry. From a structural point of view, polyvanadates may contain octahedrons VO_6, square pyramids VO_5, or tetrahedrons VO_4. They may occur either separate or mixed.
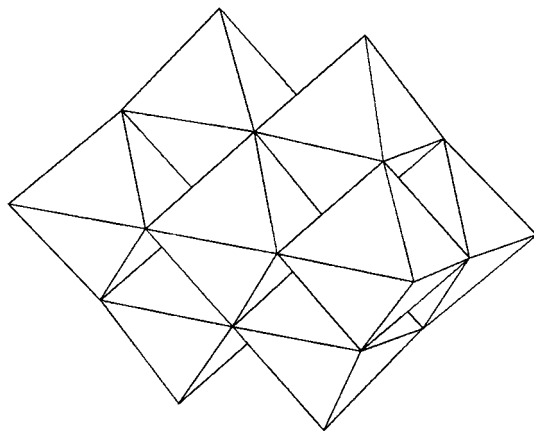
Figure 6. The isopolyvanadate $[V_{10}O_{28}]^{6-}$ which contains vanadium(V).
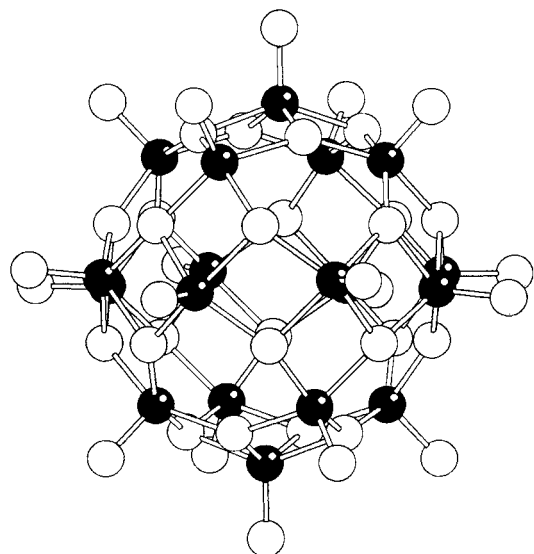
Figure 7. The isopolyvanadate $[V_{18}O_{42}]^{12-}$ which contains vanadium(IV). Black circles are vanadium atoms located in square pyramids; the vertices of which are open circle oxygen atoms.

For instance, $[V_{10}O_{28}]^{6-}$ is made of fused octahedrons (Figure 6).[9] Various names may be used: decavanadate is a trivial name just to be used as a simplified and practical name between experts when no ambiguity arises; a more complex but more accurate name is octacosaoxodecavanadate(6−) (the composition is fully given and the charge displays the occurrence of vanadium(V) only); a structural name is

di-μ_6-oxo-dodeca-μ_3-oxo-hexa-μ-oxo-octaoxo=decavanadate)(6−)

The basketlike polyvanadate $[V_{12}O_{32}]^{4-}$ which may serve as a host for acetonitrile or benzonitrile (vide infra),[10] is named following the same procedure:

octa-μ_3-oxo-dodeca-μ-oxo-dodeca(oxovanadate)(4−).

It is made only of square pyramids. A *nido* structural descriptor may be used to make it clearer:

nido-octa-μ_3-oxo-dodeca-μ-oxo-dodeca(oxovanadate)(4−)

This basket may be closed, yielding $[V_{18}O_{42}]^{12-}$ (Figure 7).[11] However it contains vanadium(IV) instead of vanadium(V). All vanadium surroundings are square pyramids. Each vanadium atom has a

terminal oxygen atom and each basal oxygen atom is shared between three pyramids, which leads to the following name:

  tetracosa-μ_3-oxo-octadeca(oxovanadate)(12−)

There is no need to put in the oxidation number of vanadium because it is deduced without ambiguity from the charge; however, it may be added if this is wished. The structural prefix *closo* may be added in front of the name as a geometrical descriptor for a better clarity:

  closo-tetracosa-μ_3-oxo-octadeca[oxovanadate=
  (IV)](12−)

It is easy to recognize from such a name that there are only square pyramids because 18 square pyramids make 90 oxygen atoms from which one substracts 18 terminal oxygen as shown by the name. Thus 72 oxygen are left which fits with 24 μ_3-oxo.

III.6. Mixed-Metal Polyoxometalates

A good example is once again provided by the Lindqvist structure. One or several tungsten atoms may be substituted by niobium or/and vanadium.[12] In such a case, the various metal atoms are named by using their element name cited in alphabetical order; they are enclosed in parentheses and the ending ate is added after the parenthesis without hyphen. Alternatively one could use a o ending to the stem of the metal cited first, and a ate ending at the stem of the metal atom cited last. The advantage of the first system which is recommended is to give a symmetrical treatment to the various metal species. A multiplicative prefix is given to each metal species; mono may be omitted if it does not create ambiguity.

Thus [NbW$_5$O$_{19}$]$^{3-}$ is named:

  μ_6-oxo-dodeca-μ-oxo-hexaoxo(niobiumpenta=
  tungsten)ate(3−)

In the case of several metal atoms of different kind, locants must be used since several isomers are possible. This implies a previous numbering of the metal skeleton following the rules stated in Section II.2.

[Nb$_4$W$_2$O$_{19}$]$^{6-}$ has two isomers trivially called cis and trans. This is a misuse of stereochemical descriptors which usually refer to the surrounding of a metal center. Assume a substitution of ligands occurs at the same time and an ambiguity will arise. It is much better to use locants.

  μ_6-oxo-dodeca-μ-oxo-hexaoxo(tetraniobium-1,2-
  ditungsten)ate(6−)

  μ_6-oxo-dodeca-μ-oxo-hexaoxo(tetraniobium-1,6-
  ditungsten)ate(6−)

Care must be exercised when using the following rule: names of metal atoms are listed in alphabetical order, but the numbering of metal atoms is ruled by Table 2, a common practice in inorganic nomenclature. The lowest locant is given to the atom coming first in Table 2. Although it may look odd to have two systems running together, this originates from the fact that symbols and names are not always based on the same root (e.g., mercury and Hg), and in the fact that symbols are universally used while element names may change from one language to another. It would be puzzling to change the numbering by translating a name.
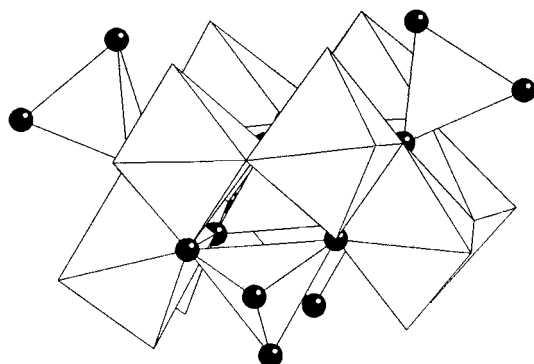
Figure 8. [V$_5$Mo$_8$O$_{40}$]$^{7-}$ made of one central VO$_4$ tetrahedron surrounded by four dinuclear Mo$_2$O$_{10}$ groups connected by outer tetrahedrons VO$_4$ at the vertices of which are shown oxygen atoms as black circles.

Another example is given by the two isomers of [V$_2$W$_4$O$_{19}$]$^{4-}$:

  μ_6-oxo-dodeca-μ-oxo-hexaoxo(tetratungsten-5,6-
  divanadium)ate(4−)

  μ_6-oxo-dodeca-μ-oxo-hexaoxo(tetratungsten-3,5-
  divanadium)ate(4−)

The order of citation of tungsten and vanadium is alphabetical, but the numbering is from the application of Table 2, tungsten atoms are given lowest possible locants.

Similarly for the hypothetical compound [NbVW$_4$=O$_{19}$]$^{4-}$.

  μ_6-oxo-dodeca-μ-oxo-hexaoxo(5-niobiumtetra=
  tungsten-3-vanadium)ate(4−)

More complicated species may be named by following the same practice. [V$_5$Mo$_8$O$_{40}$]$^{7-}$ is made of four dinuclear units of molybdenum octahedrons sharing one edge and arranged around a VO$_4$ tetrahedron (Figure 8).[13] It is a μ_8 tetrahedral ligand because one common vertex of each dinuclear unit is a tetrahedron vertex. Dinuclear units are bound together by another shared edge making a eight octahedron puckered ring. In addition each dinuclear molybdenum group has two terminal oxygen atoms which are at the edge of another VO$_4$ tetrahedron; such a tetrahedral vanadate then is a μ_4 ligand. Thus the name is written as

  μ_8-(tetraoxovanadato-O,O',O'',O''')-tetrakis(μ_4-
  tetraoxovanadato-O,O')-tetrakis[μ-oxo-
  bis(dioxomolybdate)](7−)

III.7. Nitrosylated and Analogous Compounds

The most simple compound certainly is [Mo$_6$O$_{18}$=(NO)]$^{3-}$ in which one nitrosyl ligand has substituted one terminal oxygen atom (Figure 9).[14]

  nitrosyl-μ_6-oxo-dodeca-μ-oxo-pentaoxohexa=
  molybdate(3−)

It may not seem necessary to bother about the oxidation state of the molybdenum ligated to nitrosyl since this is clearly reflected by the charge indicated in the name. It may however be stated considering different types of metal centers listed in increasing order of oxidation numbers, hence molybdenum(II) is assigned number 1.

  1a-nitrosyl-μ_6-oxo-dodeca-μ-oxo-pentaoxo[1-
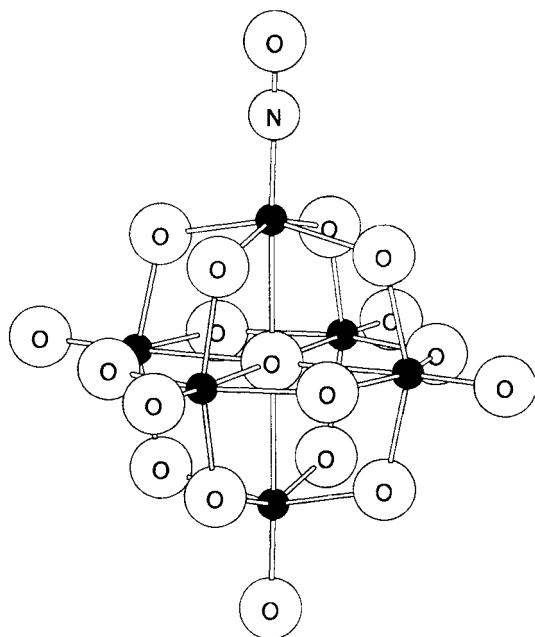 molybdenum(II)pentamolybdenum(VI)])ate(3−)

Figure 9. $[Mo_6O_{18}(NO)]^{3-}$ deriving from the Lindqvist structure by substituting one oxo ligand by one nitrosyl ligand represented on the uppermost molybdenum atom. Molybdenum atoms are black circles; the chemical symbols of nitrogen and oxygen are shown inside open circles.

Corner assignment priority is lower than central atom numbering priority. The locant 1a shows that nitrosyl is terminal and ligated to molybdenum number 1.

Dimethyl sulfate methylates such a species on a μ_2 oxygen in cis position with respect to the nitrosyl ligand.[15] The numbering of vertices is needed to identify the methoxo position:

1d-μ-methoxo-1a-nitrosyl-μ_6-oxo-undeca-μ-oxo-pentaoxohexamolybdate($2-$)

1d for methoxo and not 1b is ruled by the locant assignment of O which has priority over this of OCH$_3$.

A nitrosyl species has been made[14] which contains only five molybdenum atoms, deriving from the Lindqvist structure by loss of a MoO group opposite to the MoNO group with respect to the μ_6-oxo ligand (Figure 10a):

1b,1c,1d,1e-tetra-μ-methoxo-1a-nitrosyl-μ_5-oxo-tetra-μ-oxo-octaoxopentamolybdate($3-$)

This pentanuclear unit may be used as a block to build various compounds where it may be considered as a ligand. For instance, rhodium may ligate to two oxygen atoms. $[Rh\{C_5(CH_3)_5\}(H_2O)\{Mo_5O_{13}(OCH_3)_4=(NO)\}]^-$ is (Figure 10b)[16]

aqua(pentamethylcyclopentadienyl)[1b,1c,1d,1e-tetra-μ-methoxo-1a-nitrosyl-μ_5-oxo-tetra-μ-oxo-octaoxopentamolybdato-O,O']rhodium($1-$)

However this does not say which oxygen atoms are ligated to rhodium. Is it a four-membered ring RhOMoO or a six-membered ring RhOMoOMoO? The use of locants for ligating oxygen atoms makes the name clear and complete:

aqua(pentamethylcyclopentadienyl)(1b,1c,1d,1e-tetra-μ-methoxo-1a-nitrosyl-μ_5-oxo-tetra-μ-oxo-octaoxopentamolybdato-O^{2f},O^{3f})rhodium($1-$)

The same type of compound may be prepared with silver. Two silver atoms get a square-planar envi-

ronment of four oxygen atoms without any silver–silver bond, what implies two Mo$_5$ units:[17]

bis(1b,1c,1d,1e-tetra-μ-methoxo-1a-nitrosyl-μ_5-oxo-tetra-μ-oxo-octaoxopentamolybdato)-$O^{2f},O^{3f};O^{4f},O^{6f}$-disilver($4-$)

A more complicated species is prepared with nickel. It contains a core of four octahedrons, two nickel containing and two molybdenum containing, $[Mo_2=Ni_2(OH)_2\{Mo_5O_{13}(OCH_3)_4(NO)\}_2(CH_3OH)_4(NO)_2]^{2-}$. The two nickel ones share an edge with two μ-hydroxo bridges. Each nickel-containing octahedron shares with one molybdenum octahedron a face at the vertices of which are one hydroxo and two methoxo ligands. Each molybdenum is bound to an Mo$_5$(NO) polyoxometalate ligand as in the preceding rhodium complex (Figure 10c).[17] Thus the name is

di-μ_3-hydroxo-tetra-μ-methanol-dimethanol=dinitrosylbis(1b,1c,1d,1e-tetra-μ-methoxo-1a-nitrosyl-μ_5-oxo-tetra-μ-oxo-octaoxopenta=molybdato-O^{2f},O^{3f})(dimolybdenumdinickel)ate($2-$)

This does not say which ligands are bound to nickel and which ligands are bound to molybdenum in the four metal Mo$_2$Ni$_2$ core. These metal atoms have to be numbered, 1 and 2 for nickel, 3 and 4 for molybdenum following the sequence of Table 2. By introducing the κ notation, everything is given to reconstruct the structure from the name. Be careful that two completely independent numberings are running altogether is such a name, the numbering of the Mo$_2$Ni$_2$ core and the numbering of the Mo$_5$-(NO) ligand.

di-μ_3-hydroxo-1:2:3κO,1:2:4κO-tetra-μ-methanol-1:3κO,2:3κO,1:4κO,2:4κO-dimethanol-1κO,2κO-dinitrosyl-3κN,4κN-bis(1b,1c,1d,1e-tetra-μ-methoxo-1a-nitrosyl-μ_5-oxo-tetra-μ-oxo-octaoxo=pentamolybdato)-3κO^{2f},3κO^{3f};4κO^{2f},4κO^{3f}-(dimolybdenumdinickel)ate($2-$)

The same type of substitution occurs with an imidato ligand. Phenylimidato provides an example:[18] an imidato-containing species $[Mo_6O_{17}(NC_6H_5)_2]^{2-}$ has been prepared where the two substituted sites are two terminal oxygen atoms attached to two adjacent molybdenum octahedrons. The assignment of locants is needed:

μ_6-oxo-dodeca-μ-oxo-tetraoxo-5d,6f-bis[phenyl=imidato($2-$)]hexamolybdate($2-$)

5d,6f are required because the ligating atom N comes after O in Table 2, rule 5b.

A diimidato ligand may behave as a bridge between two hexamolybdates:[19]

μ-[cyclohexyl-1,4-diimidato($2-$)]-6fκN,6'fκN-bis(μ_6-oxo-dodeca-μ-oxo-pentaoxohexa=molybdate)($4-$)

6f points out the ligated site of the hexamolybdate. The ($2-$) after imidato is needed to indicate that the ligand has lost two H$^+$.

Recently, very large polyoxomolybdates made of Mo$_{17}$ building blocks have been prepared. There are compounds containing two such blocks, or three, or even six assembled together around some other metal atoms.[20]

It is tempting to use this system of nomenclature to give them a name. Let us take the case of $[Mo_{36}=O_{108}(NO)_4(H_2O)_{16}]^{12-}$ (Figure 11). It may be described
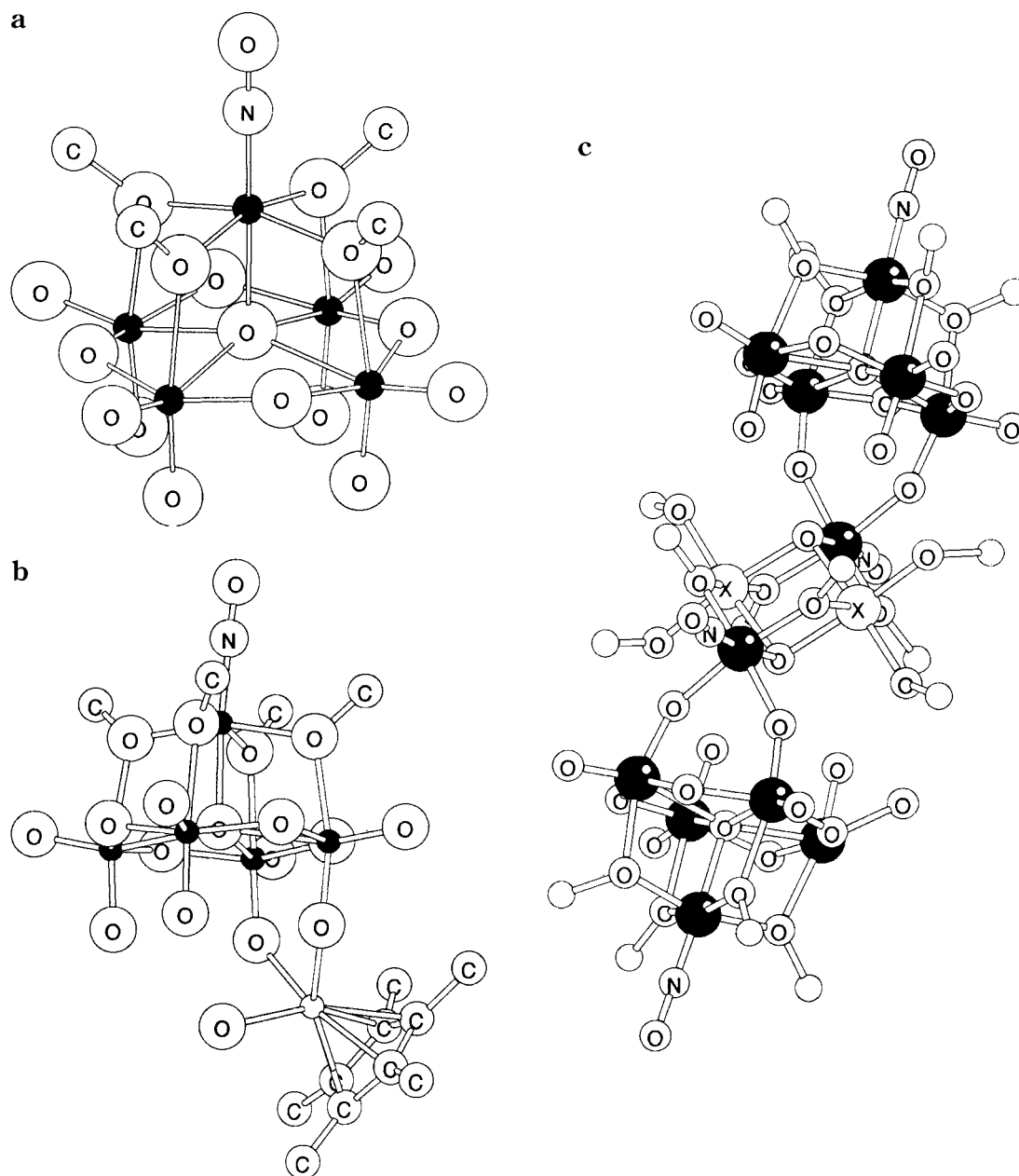
Figure 10. (a) $[Mo_5O_{13}(OCH_3)_4(NO)]^{3-}$ deriving from the preceding by removal of one MoO group and substituting four oxo ligands by four methoxo ligands. Molybdenum atoms are black circles; the chemical symbols of nitrogen, oxygen, and carbon are shown inside open circles. (b) $[Rh\{C_5(CH_3)_5\}\{Mo_5O_{13}(OCH_3)_4(NO)\}(H_2O)]^-$ in which the fragment aquacyclopentadienylrhodium fragment is bound to two oxygen atoms. Molybdenum atoms are black circles; the chemical symbols of nitrogen, oxygen, and carbon are shown inside open circles. Rhodium is shown as a small open circle without symbol. (c) $[Mo_2Ni_2(OH)_2\{Mo_5O_{13}(OCH_3)_4(NO)\}_2(CH_3OH)_4(NO)_2]^{2-}$ containing two ligands $[Mo_5O_{13}(OCH_3)_4(NO)]^{3-}$. Molybdenum atoms are black circles; the chemical symbols of nitrogen, oxygen are shown inside open circles. Carbon atoms are small open circles without symbol. X inside a large open circle represents nickel atoms.

as two Mo_{17} building blocks connected by two independent MoO_6 octahedrons. The first problem to solve is to name the block $Mo_{17}O_{48}(NO)_2(H_2O)_8$ which contains six types of molybdenum surroundings (Figure 12). One may just name the various types of ligands with their bridging feature:

di-μ-aqua-hexaaquadinitrosyldi-μ_4-oxo-deca-μ_3-oxo-tetradeca-μ-oxo-octacosaoxoheptadeca=
molybdate

It seems better to name the two independent MoO_6 as bridging two Mo_{17} blocks rather than the opposite, thus the name is

bis(μ-hexaoxomolybdato-$O,O':O'',O'''$)-bis(di-μ-
aqua-hexaaquadinitrosyldi-μ_4-oxo-deca-μ_3-oxo-

tetradeca-μ-oxo-tetracosaoxoheptadeca=
molybdate)(12−)

A more accurate name is cast by numbering molybdenum atoms in the Mo_{17} unit using rules stated in section II.2. The price to pay is an increased length of the name but all the details needed to reconstruct the structure are included.

bis(μ-hexaoxomolybdato)-$O^{1,1'},O^{2,2'};O^{3,3'},O^{6,6'}$-
bis(10.13,11.12-di-μ-aqua-1,2,3,4,5,6-hexaaqua-
7,8-dinitrosyl-7.9.14.15,8.9.16.17-di-μ_4-oxo-
1.3.7,1.4.7,2.5.8,2.6.8,3.7.14,4.7.15,5.8.16,=
6.8.17,9.14.17,9.15.16-deca-μ_3-oxo-3.10,4.11,=
5.12,6.13,7.9,8.9,10.13,10.14,11.12,11.15,12.16,=
13.17,14.17,15.16-tetradeca-μ-oxo-
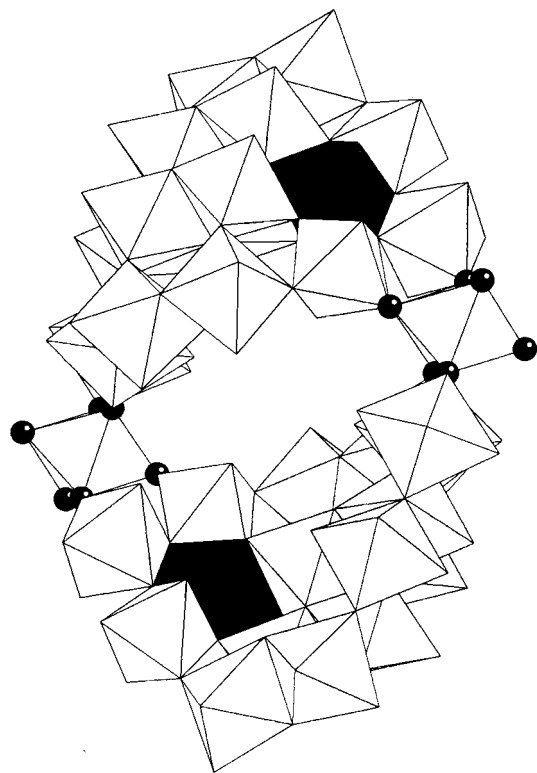
Figure 11. Polyhedral representation of $[Mo_{36}O_{108}(H_2O)_{16}=(NO)_4]^{12-}$. It shows the two identical Mo_{17} units, each one containing a black pentagonal square pyramid one upper vertex of which is occupied by a nitrosyl group. They are connected by two MoO_6 octahedrons the oxygen atom vertices of which are shown as black circles.

  1,1,2,2,3,4,4,5,5,6,10,10,11,11,12,12,13,13,14,=
  15,16,17-docosaoxoheptadecamolybdate)(12−)

In such a name, 10.13,11.12-di-μ-aqua means that there are two bridging molecules of water, one bridging molybdenum atoms 10 and 13, one bridging molybdenum atoms 11 and 12, and similarly all throughout the name.

   Other polyoxometalates of this type may be named similarly. For instance, $[Mo_{57}V_6O_{180}(OH)_3(NO)_6=(H_2O)_{18}]^{24-}$ is a three Mo_{17} building blocks named as above and assembled in a ring; this is shown by *cyclo*-tris in the name. They are connected by three complex bridges. Each bridge is made of one $Mo_2O_6=(\mu\text{-}OH)(\mu\text{-}H_2O)_2$ dinuclear unit and two $VO_5(H_2O)$ octahedrons which will be treated as ligands; each bridging group is bound to four molybdenum atoms, two of the right Mo_{17} unit, and two of the left Mo_{17} unit; this is shown by μ_4-(....-O,O',O',O'') in the name:

  cyclo-tris{bis-μ_4-(aquapentaoxovanadato-
  O,O',O',O'')-μ_4-[di-μ-aqua-μ-hydroxo-
  bis(trioxomolybdato)-$O,O':O',O''$]-(diaqua=
  dinitrosyldi-μ_4-oxo-deca-μ_3-oxo-tetradeca-μ-oxo-
  icosaoxoheptadecamolybdate)}(24−)

III.8. The Anderson Structure and Derived Compounds

   The Anderson structure may be described as an isopolyoxometalate containing a crown of six octahedrons sharing edges. The center may be occupied or not.
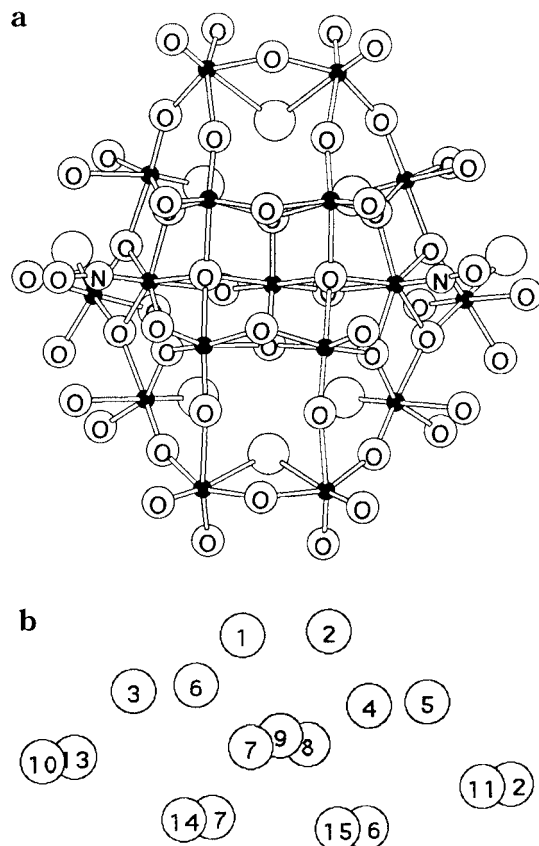
Figure 12. (a) Projection of $Mo_{17}O_{52}(NO)_2(H_2O)_8$ showing the various types of oxygen atoms. Small black circles are molybdenum atoms; the symbols of oxygen and nitrogen atoms are shown inside open circles; large open circles are water molecules. (b) Molybdenum framework of the Mo_{17} group showing the numbering of molybdenum atoms. The reference axis is vertical and goes through Mo9. The reference plane contains the reference axis; it is parallel to the sheet of paper. Atoms 1, 3, 4, 7, 10, 11, 14, 15, are above this reference plane; atoms 2, 5, 6, 8, 12, 13, 16, 17 are below the reference plane.

III.8.1. Oxo Ligands

   The first compound which has been described with such a structure contains a metal atom at the center of the crown which then has a octahedral surrounding and which shares six oxygen atoms with the crown (Figure 13). This central atom may be a transition metal, chromium, iron, cobalt, platinum, or a main group element, zinc, gallium, tellurium-(VI), [21] iodine(VII). The polyanion has a ternary axis and the formula is $[MM'O_{24}]^{n-}$. An isomer $[Mo_7O_{24}]^{6-}$ occurs which has C_{2v} symmetry. Citing all the oxygen atoms leads straightforwardly to the structure of $[TeMo_6O_{24}]^{6-}$. A strict application of coordination compounds nomenclature rules requires an alphabetical sequence of symbols for cations, i.e. Mo_6-Te; however due to a long practice and to the easy replacement of the central atom, tellurium in this case, by an element for which the alphabetical sequence is changed, e.g. iodine, the general formula $[XMo_6O_{24}]^{6-}$ is preferred:

  hexa-μ_3-oxo-hexa-μ-oxo-dodecaoxo(hexa=
  molybdenum-7-tellurium)ate(6−)
or
  hexa-μ_3-oxo-hexa-μ-oxo-[hexakis(dioxo=
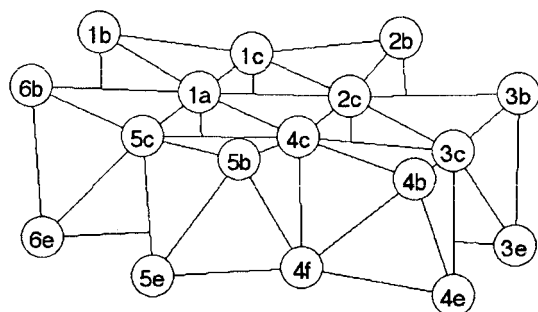 molybdenum)-7-tellurium]ate(6−)

Figure 13. The seven fused octahedrons of the Anderson structure with the numbering of some octahedron corners. The reference axis is vertical and goes through the metal atom located at the center of the central octahedron, shown by its three upper corners 1a, 2c, and 4c. The reference plane contains the reference axis and three metal atoms, located respectively at the centers of octahedrons shown by their upper faces, 1a, 1b, 1c, and 1a, 2c, 4c, and 3c, 4b, 4c.

The locant 7 indicates the position of tellurium. Since the central cavity may be empty, the numbering starts with the crown and finishes with the center of the cavity. The name of the C_{2v} isomer $[Mo_7O_{24}]^{6-}$ is (see section III.4)

di-μ_4-oxo-di-μ_3-oxo-octa-μ-oxo-dodecaoxohepta=
molybdate)(6−)

In the case of the chromium-containing structure there are six hydrogen atoms, the positions of which are considered to be the six OH groups bridging the central atom to the molybdenum-containing crown octahedrons:

hexa-μ_3-hydroxo-hexa-μ-oxo-[7-chromiumhexa=
kis(dioxomolybdenum)]ate(6−)

The oxidation state of chromium may be easily deduced from the charge since it is well known that there usually is molybdenum(VI). However, to point it out, one may write:

hexa-μ_3-hydroxo-hexa-μ-oxo-[7-chromium(III)=
hexakis(dioxomolybdenum)]ate(6−)

If it is preferred not to show the location of the hydrogen atoms, treating them as acidic hydrogen atoms of an oxoanion, the name is

hexahydrogenhexa-μ_3-oxo-hexa-μ-oxo-[7-
chromium(III)hexakis(dioxomolybdenum)]ate(6−)

III.8.2. Mixed-Ligand Compounds

The crown may have an empty central cavity. In such a case, ligands are capping this empty cavity on both sides of the crown.

This capping ligand may be a tetraoxoarsenate(V) AsO_4^{3-}, or a tetraoxomolybdate(VI) MoO_4^{2-}, or a methyltrioxoarsonate(V) $C_6H_5AsO_3^{3-}$. Names are

bis-μ_6-(tetraoxoarsenato-O,O',O'')-hexa-μ-oxo-
hexakis(dioxomolybdate)(6−)
bis-μ_6-(methyltrioxoarsonato-O,O',O'')-hexa-μ-
oxo-hexakis(dioxomolybdate)(4−)[22]
bis-μ_6-(tetraoxomolybdato-O,O',O'')-hexa-μ-oxo-
hexakis(dioxomolybdate)(4−)

The two tetrahedrally surrounded molybdenum atoms could be as well included into the metal framework which would then count eight molybdenum atoms. Treating MoO_4 as a ligand produces a simpler name, makes clear the structural relationship, and thus is preferred (Figure 14).
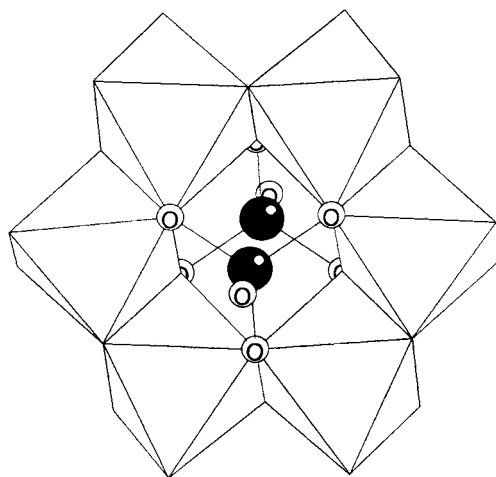
Figure 14. The octamolybdate $[Mo_8O_{26}]^{4-}$ made of a crown of six fused MoO_6 octahedrons sharing edges and of two MoO_4 tetrahedrons, one on each side of the crown. These tetrahedrons are shown by black circles which are molybdenum atoms, and by open circles with inside the symbol of oxygen.
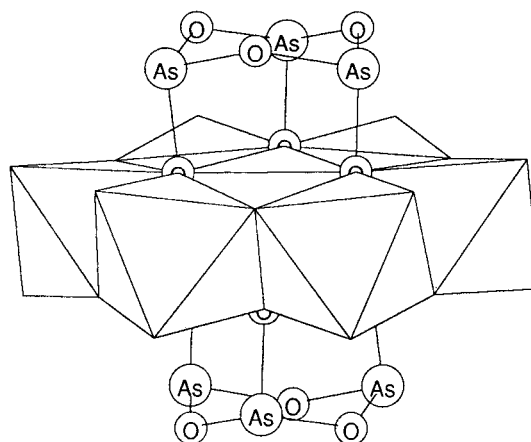

Figure 15. $[CoW_6O_{24}(As_3O_3)_2]^{4-}$ showing the crown of six WO_6 octahedrons enclosing one cobalt atom with two cyclotriarsenite(3−) ligands, one on each side of the crown. Arsenic and oxygen atoms are shown by their symbols.

There is an Anderson structure based on a CoW_6 skeleton with two cyclotriarsenite, one on each side of the crown, $[CoW_6As_6O_{30}]^{4-}$ (Figure 15).[23]

The oxygen atoms of each cyclohexaoxotriarsenate-(III) bridge the six tungsten atoms (or molybdenum) of the crown and the central cobalt octahedron. Thus this arsenic containing ligand is μ_7.

hexa-μ-oxo-bis-μ_7-[tri-μ-oxotris(oxoarsenato)(III)-
O,O',O'')]-[7-cobalthexakis(dioxotungsten)]ate(4−)

Those two features, an occupied central position and a capping ligand, may be found in some other compounds. An example is $[MnMo_6O_{18}\{CH_3C=(CH_2O)_3\}_2]^{3-}$ which contains a capping triol (Figure 16a).[24]

bis-μ_7-(neopentane-1,2,3-triolato-O,O',O'')-
hexa-μ-oxo-[7-manganese(III)hexakis(dioxo=
molybdenum)]ate(3−)

The triol caps three molybdenum octahedrons and the central manganese containing octahedron; there is one triol on each side.

There is an isomer $[ZnMo_6O_{18}\{CH_3C(CH_2O)_3\}_2]^{4-}$ for which the CH_3C axis of the triol is not any longer

a

b

c
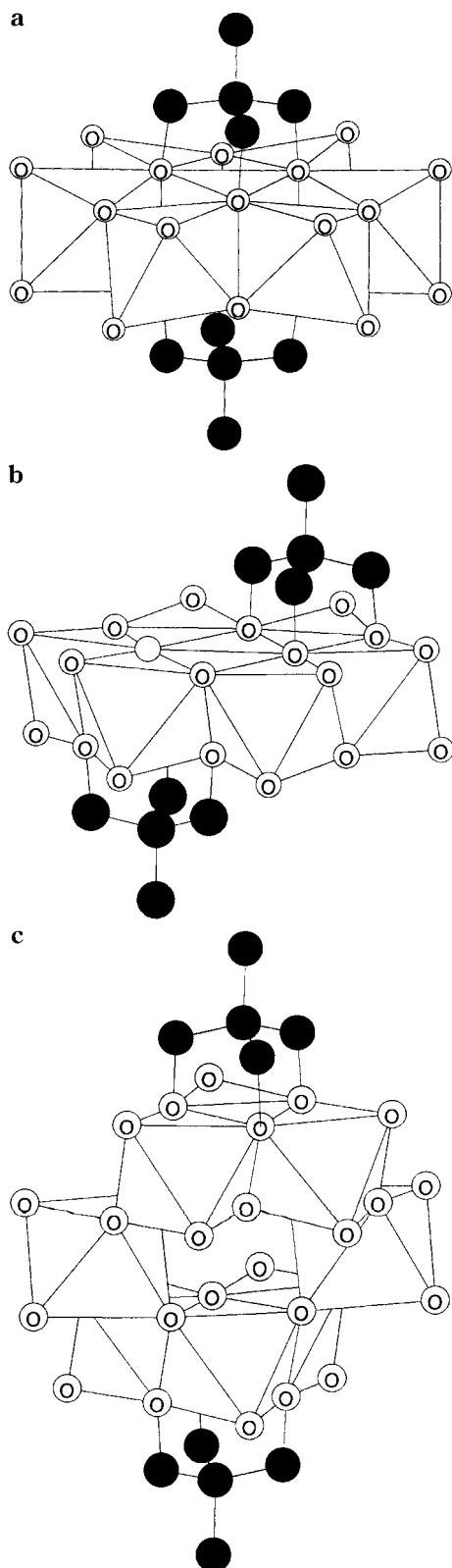
Figure 16. (a) $[MnMo_6O_{18}\{CH_3C(CH_2O)_3\}_2]^{3-}$ is the same type of compound as this of Figure 15 with a triolate instead of a triarsenite(3−). Carbon atoms are shown by black circles. (b) $[Mo_6ZnO_{18}\{CH_3C(CH_2O)_3\}_2]^{4-}$ is the same type of compound as this of Figure 16a but the triolate is out of the center of the surface of the heptametalate. The open circle is an OH group; there are two of them symmetrically located. (c) $[Mo_8O_{24}\{CH_3C(CH_2O)_3\}_2]^{6-}$ showing eight fused octahedrons with two triolates, one over the upper three molydenum group, the other under the lower three molybdenum group. Oxygen atoms are shown by the symbol O inside an open circle, carbon atoms are black.

the ternary axis of the Anderson basic structure but it is parallel to it (Figure 16b).[24] Thus the triol is now capping five octahedrons, one zinc containing and four molybdenum containing, and it is out of the center of the Anderson basic structure surface:

bis-μ_5-(neopentane-1,2,3-triolato-O,O',O'')-di-μ_3-oxo-tetra-μ-oxo-[hexakis(dioxomolybdenum)-7-zinc]ate(4−)

Another compound $[Mo_8O_{24}\{CH_3C(CH_2O)_3\}_2]^{6-}$ containing the same triol now capping three edge-sharing molybdenum octahedrons is known (Figure 16c).[24] Two triol−Mo₃ units are connected by two molybdenum containing octahedrons sharing edges with the preceding units. A name may be given in which the eight octahedrons are treated as the frame of the polyoxometalate:

bis-μ_3-(neopentane-1,2,3-triolato-O,O',O'')-di-μ_3-oxo-octa-μ-oxo-tetradecaoxooctamolybdate(6−)

Such a name is a bit obscure to rebuild the structure. Another method would be to treat both MoO₆ octahedrons joining the two triol−Mo₃ units as bridging ligands which leads to the following name:

bis(μ_4-hexaoxomolybdato-O,O',O'',O''')-bis[μ_3-(neopentane-1,2,3-triolato-O,O',O'')-μ_3-oxo-pentaoxotrimolybdate](6−)

This name has the advantage of pointing out that there are two equivalent triol−Mo₃ units connected by two MoO₆ octahedrons, each of them being connected to four different molybdenum atoms by four different oxygen atoms.

III.9. Sulfur-Containing Compounds

This type of compound does not raise any new problem.

The Lindqvist structure compound $[W_6O_{18}S]^{2-}$

μ_6-oxo-dodeca-μ-oxo-pentaoxothiohexa=tungstate(2−)

contains one terminal sulfur atom,

μ_6-oxo-undeca-μ-oxo-μ-thio-hexakis(oxo=tungstate)(2−)

contains one bridging sulfur atom. The name

μ_6-oxo-dodeca-μ-oxo-pentaoxo-1a-thio(6-niobiumpentatungsten)ate(3−)

refers to a compound which contains one terminal sulfur atom bound to a tungsten atom on a position symmetrical to niobium with respect to the μ_6-oxygen atom. Metal numbering has priority over ligand numbering.

Another example is given by $[W_3OS_8]^{2-}$ (Figure 17a).[25] It may be named on the basis of a three tungsten polymetalate. However it contains one square pyramid bound by two basal edges to two WS₄ tetrahedrons, and the apical position of the square pyramid is occupied by oxygen. In order to make the name simpler, it seems better to treat tetrahedrons as ligands:

oxobis(tetrathiotungstato-S,S')tungstate(2−)

The same type of compound $[W_4S_{12}]^{2-}$ occurs with two square pyramids sharing one edge, each of them being bound to a tetrahedron WS₄ (Figure 17b):[26]
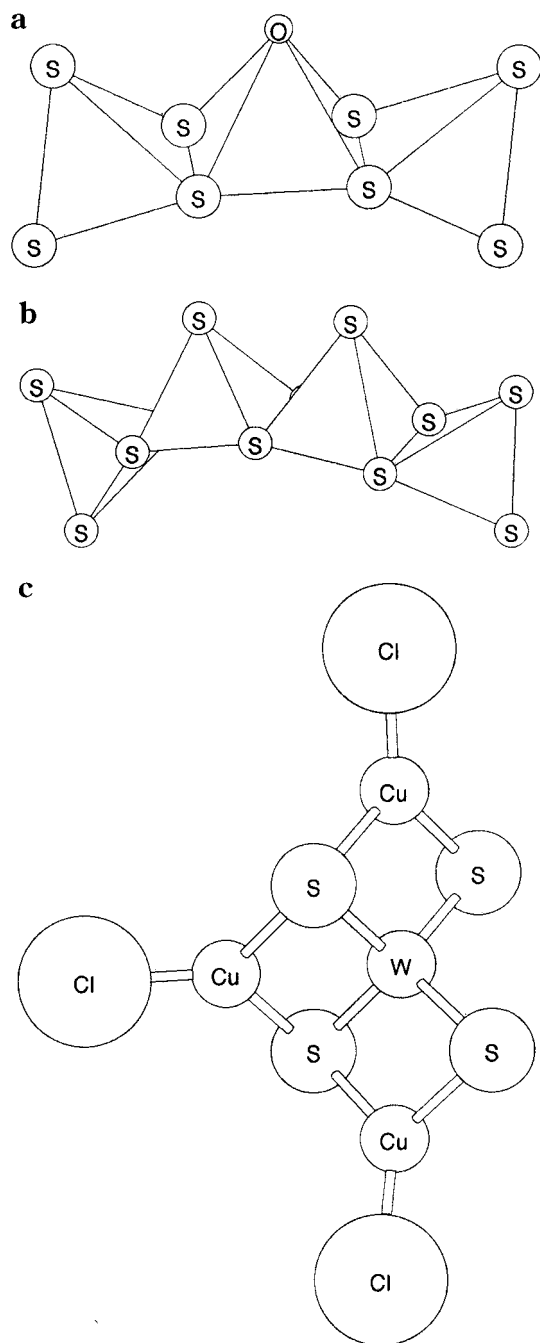
bis(tetrathiotungstato-S,S')di-μ-thio-bis(thiotungstate)(2−)

Figure 17. (a) $[W_3OS_8]^{2-}$ is made of one square pyramid and two tetrahedrons treated as ligands to the square-pyramidal tungsten atoms. Symbols of sulfur and oxygen are inside open circles. (b) $[W_4S_{12}]^{2-}$ is made of two square pyramids sharing one edge and two tetrahedrons treated as ligands to square-pyramidal tungsten atom. (c) $[Cu_3WCl_3S_4]^{2-}$ is made of three $CuWS_2$ squares sharing WS edges so that the central tunsgten atom is tetrahedally surrounded by sulfur. Symbols of the elements are written inside open circles.

Some mixed compound containing copper and tungsten may be prepared. Their names are simple to build up. For instance $[WCu_3Cl_3S_4]^{2-}$ is made of three $WCuS_2$ squares sharing edges (Figure 17c):

di-μ_3-thio-di-μ-thio-[tris(chlorocopper)=
tungsten]ate(2−)

A dicubane structure $[Cu_4W_2Cl_4S_8]^{2-}$ is not more difficult to name:[27]
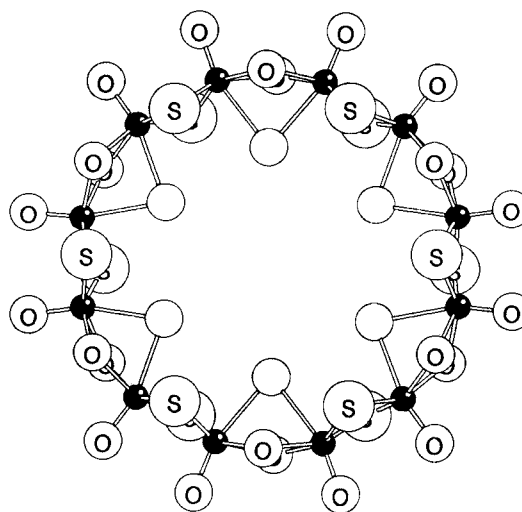
Figure 18. The cyclic hexamer $[Mo_{12}O_{24}S_{12}(H_2O)_6]$. Black circles are molybenum atoms. Symbols of oxygen and sulfur atoms are inside open circles. Open circles without symbols are water molecules.

di-μ_4-thio-tetra-μ_3-thio-[tetrakis(chlorocopper)=
bis(thiotungsten)]ate(2−)

As long as the structure is symmetrical and does not not raise any special assignment, the name is found in a straightofrward manner. For example, $[Mo_{12}O_{24}S_{12}(H_2O)_6]$ is a cyclic hexamer (Figure 18) based upon the $O=Mo(\mu\text{-}O)_2(\mu\text{-}H_2O)Mo=O$ fragment bridged on each side by two sulfur atoms:[28]

cyclo-hexakis{di-μ-thio-[μ-aqua-di-μ-oxo-
bis(oxomolybdate(VI)]}

III.10. Host–Guest Compounds

The concept of host−guest compounds has been recently introduced to explain the association of two molecules, charged or not, one being much smaller than the other, the small one being sometimes incorporated inside a closed structure.

It is proposed to name such compounds as follows. The two names of the guest and of the host are cited in this order, because the host may remain the same while the guest may change. Their names are kept as they stand when alone. The guest is introduced by the stereochemical descriptor *crypto* written in italics before the name of the guest and separated by an hyphen. Guest and host are separated by a large dot as it is recommended for addition compounds. Each unit, guest and host, keeps its own electrical charge. This method has the advantage to designate immediately to the reader the host−guest situation. Separating the names cited as they stand for the compound alone keeps unchanged the host name, regardless of the guest. For instance, the association of CH_3CN with $[V_{12}O_{32}]^{4-}$ is named:[10]

crypto-acetonitrile·octa-μ_3-oxo-dodeca-μ-
oxo-dodecakis(oxovanadate)(4−)

Similarly $[H_4V_{18}O_{42}]^{8-}$ enclosing either a chloride or a water molecule will be[29,54]

crypto-aqua·tetrahydrogentetracosa-μ_3-oxo-
octadecakis(oxovanadate)(8−)

crypto-chloride·tetrahydrogentetracosa-μ_3-oxo-
octadecakis(oxovanadate)(8−)

Taking a different type of compounds, $[Na_2Fe_{18}S_{30}]^{8-}$, the two structurally different host−guest sodium containing polythioferrates will be named[30]

crypto-disodium·dodeca-μ_3-thio-octadeca-μ-thio-octadecaferrate(10−)

crypto-disodium·di-μ_4-thio-octa-μ_3-thio-icosa-μ-thio-octadecaferrate(10−)

IV. Heteropolyanions

Heteropolyanions are those polyanions and their derivatives made of an assembly of fused MO_6 octahedrons more or less completely wrapped around a tetrahedron containing traditionally a main group element, more seldomly a transition metal.

IV.1. The Keggin Structure and Its Isomers

The first polyanion prepared by Berzelius[31] was a phosphomolybdate $[PMo_{12}O_{40}]^{3-}$. The structure of a similar compound, i.e., $[PW_{12}O_{40}]^{3-}$, was determined about 100 years later using X-ray diffraction by Keggin.[32] The structure determination demonstrated that a former proposal based on speculation was incorrect. The structure was so new and appeared so complicated that the name "Keggin" for this polytungstate and for the series $[XM_{12}O_{40}]^{n-}$ was born. X may be B, Si, Ge, P^V, As^V, and some other atoms. M is either molybdenum or tungsten. Several names have been used, besides the trivial name "Keggin compound". For instance, $[SiW_{12}O_{40}]^{4-}$ has been named either silicotungstate, or tungstosilicate, or silicododecatungstate, or 12-tungstosilicate. It seems better to use the ending tungstate because it is a polyoxometalate, i.e., a polyoxotungstate, and because the central atom may be easily changed, or even be missing.

More complete names should describe the content. Today the structure shown in Figure 19 is known. Four M_3O_{13} groups are arranged around the heteroatom which is tetrahedrally surrounded. A M_3O_{13} group is an assembly of three octahedrons sharing edges so that they have a common corner which is also a corner of the central tetrahedron. Due to the easy substitution of this central atom, the central tetrahedron will be treated as a μ_{12} bridging ligand. Two M_3O_{13} share two corners. Thus a name based on the formula is

hexatriacontaoxo(tetraoxosilicato)dodeca= tungstate(4−)

Ligands, oxo and tetraoxosilicato, are cited in alphabetical order.

Such a name does not allow to reconstruct the structure. It is is necessary to give more details. A more precise approach would be to describe the features of the various oxygen atoms.

tetracosa-μ-oxo-dodecaoxo-μ_{12}-tetraoxosilicato-dodecatungstate(4−)

or

tetracosa-μ-oxo-μ_{12}-tetraoxosilicato-dodecakis= (oxotungstate)(4−)

However which oxygen atom is bound to which metal atom cannot be found with such a name. Deep thought is necessary to reconstruct the structure. The next level will be to designate the bridges by a
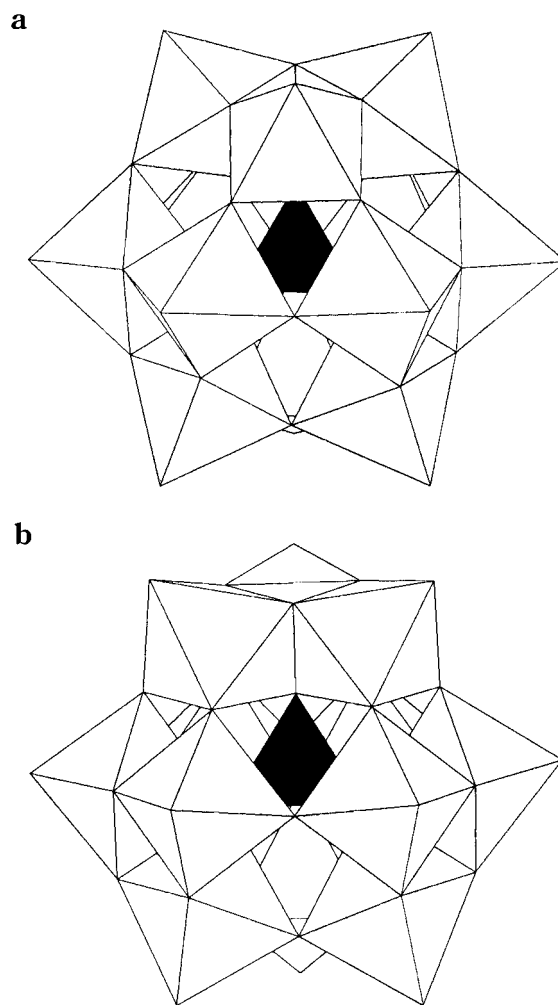
Figure 19. Drawing showing the fusion of 12 octahedrons. Isomer 1 has T_d symmetry (*a*), isomer 2 has C_{3v} symmetry after rotation of one M_3O_{13} group located at the top of the polyanion (*b*). The heteroatom containing central tetrahedron is black.

sequence of locants which requires the numbering of tungsten atoms following rules of stated in section II.2:

1.2,1.3,1.4,1.9,2.3,2.5,2.6,3.7,3.8,4.5,4.9,4.10,= 5.6,5.10,6.7,6.11,7.8,7.11,8.9,8.12,9.12,10.11,= 10.12,11.12-tetracosa-μ-oxo-μ_{12}- (tetraoxosilicato-$O^{1.4.9}, O^{2.5.6}, O^{3.7.8}, O^{10.11.12}$)- dodecakis(oxotungstate)(4−)

The final level of complexity is to name each bridging oxygen corner which has two locants depending on the considered octahedron (Figure 20). Thus the oxygen atom joining tungsten atoms 1 and 4 is 1e and 4a so that the bridge is designated by 1e.4a-μ-oxo. The most complete and most precise name, but of course also longer and cumbersome, is

1c.2b,1b.3c,1e.4a,1d.9a,2c.3b,2d.5a,2e.6a,3d.7a,= 3e.8a,4c.5b,4d.9e,4f.10b,5e.6d,5f.10c,6c.7b,= 6f.11b,7e.8d,7f.11c,8c.9b,8f.12b,9f.12c,10f.11d,= 10d.12f,11f.12d-tetracosa-μ-oxo-μ_{12}- (tetraoxosilicato-$O^{1.4.9}, O^{2.5.6}, O^{3.7.8}, O^{10.11.12}$)- dodecakis(oxotungstate)(4−)

Let us mention that this name has been given to a chemist who was not very familiar with polyoxometalate chemistry. He succeeded in rebuilding the structure from the name.
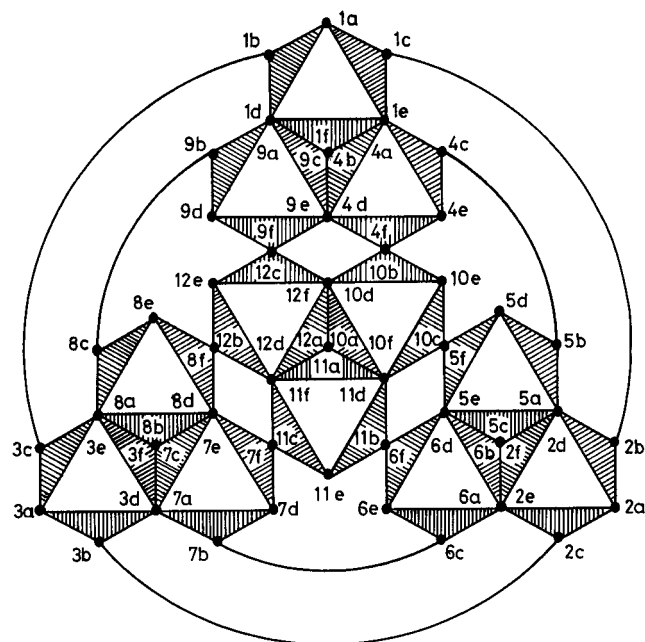
Figure 20. The Keggin structure opened with locant assignment. Circles mean that the two related vertices are fused.

Such a method has another great advantage. The structure described by Keggin is often trivially called the α-[SiW$_{12}$O$_{40}$]$^{4-}$. It has been found that a M$_3$O$_{13}$ group may be turned by 60° around its C$_3$ axis. This isomer is trivially called β-[SiW$_{12}$O$_{40}$]$^{4-}$ (Figure 20).[33] On this basis one may think about the rotation of a second, and a third, and a fourth group (Figure 21). Regardless of what those structures are hypothetical or isolated, either containing twelve metal atoms or not, one may try to name those isomers following the same principles using the same formula [SiW$_{12}$O$_{40}$]$^{4-}$ for the sake of clarity.

isomer 1, Keggin structure, T_d symmetry
1.2,1.3,1.4,1.9,2.3,2.5,2.6,3.7,3.8,4.5,4.9,4.10,=
5.6,5.10,6.7,6.11,7.8,7.11,8.9,8.12,9.12,10.11,=
10.12,11.12-tetracosa-μ-oxo-μ_{12}-
(tetraoxosilicato-$O^{1.4.9}$,$O^{2.5.6}$,$O^{3.7.8}$,$O^{10.11.12}$)-
dodecakis(oxotungstate)(4−)

isomer 2, C_{3v} symmetry, one group turned by 60°
1.2,1.3,1.4,1.9,2.3,2.5,2.6,3.7,3.8,4.5,4.9,4.10,=
5.6,**5.11**,6.7,6.11,7.8,7.12,8.9,8.12,9.10,10.11,=
10.12,11.12-tetracosa-μ-oxo-μ_{12}-
(tetraoxosilicato-$O^{1.4.9}$,$O^{2.5.6}$,$O^{3.7.8}$,$O^{10.11.12}$)-
dodecakis(oxotungstate)(4−)

isomer 3, two groups turned by 60°
1.2,**1.2**,1.4,1.5,2.3,2.6,3.6,3.7,3.9,4.5,4.7,4.10,=
5.8,$\overline{5.11}$,6.8,6.12,7.9,7.10,8.11,8.12,9.10,9.12,=
10.11,11.12-tetracosa-μ-oxo-μ_{12}-
(tetraoxosilicato-$O^{1.4.5}$,$O^{2.3.6}$,$O^{7.9.10}$,$O^{8.11.12}$)-
dodecakis(oxotungstate)(4−)

isomer 4, three groups turned by 60°
1.2,1.3,1.4,**1.6**,2.3,2.4,2.5,3.5,3.6,4.7,4.8,5.9,=
5.10,6.11,$6.\overline{12}$,7.8,7.12,7.12,8.9,8.9,9.10,10.11,=
10.11,11.12-tetracosa-μ-oxo-μ_{12}-
(tetraoxosilicato-$O^{1.2.3}$,$O^{4.7.8}$,$O^{5.9.10}$,$O^{6.11.12}$)-
dodecakis(oxotungstate)(4−)

isomer 5, four groups turned by 60°
1.2,1.3,1.4,**1.4**,2.3,2.5,2.5,3.6,3.6,4.7,4.12,5.8,=
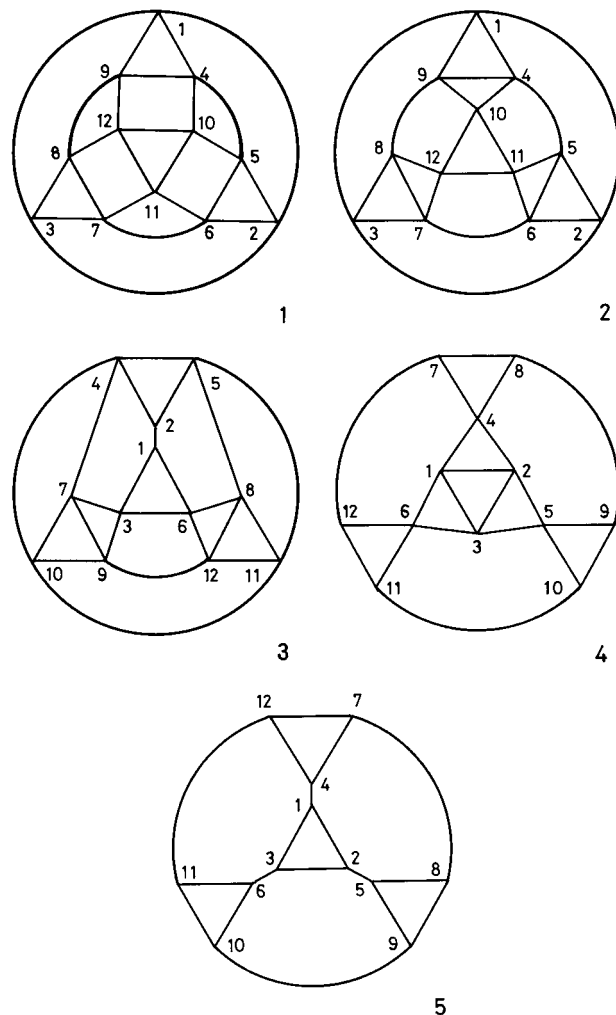5.9,6.10,$6.\overline{11}$,7.8,7.8,7.12,8.9,9.10,9.10,10.11,=

Figure 21. Five isomers of XM$_{12}$O$_{40}$, only the 12 tungsten metal atom frameworks are shown: 1 is the Keggin structure; 2 has one M$_3$O$_{13}$ group turned; 3 has two groups turned; 4 has three groups turned; and 5 has four groups turned. Numbers are locants assigned to metal atoms in each case.

11.12,11.12-tetracosa-μ-oxo-μ_{12}-
(tetraoxosilicato-$O^{1.2.3}$,$O^{4.7.12}$,$O^{5.8.9}$,$O^{6.10.11}$)-
dodecakis(oxotungstate)(4−)

In the preceding names, bold underlined locants point out the first locant difference with respect to the Keggin compound of T_d symmetry.

At this point, it should be remembered that the central position may not be occupied by an heteroatom, but by two hydrogen atom which then make two μ_3-hydroxo and two μ_3-oxo ligands.[35] The α-isomer of T_d symmetry is trivially known as the metatungstate:

1.4.9,2.5.6-di-μ_3-hydroxo-3.7.8,10.11.12-di-μ_3-
oxo-1.2,1.3,1.4,1.9,2.3,2.5,2.6,3.7,3.8,4.5,4.9,=
4.10,5.6,5.10,6.7,6.11,7.8,7.11,8.9,8.12,9.12,=
10.11,10.12,11.12-tetracosa-μ-oxo-
dodecakis(oxotungstate)(6−)

Since the two hydrogen atoms have several possibilities for attachment on the four oxygen atoms, it is also possible to name this species as an acidic polyanion. Let us mention however that those hydrogen atoms are so severely trapped in the central cavity that they cannot be titrated.

dihydrogen-1.4.9,2.5.6,3.7.8,10.11.12-tetra-μ_3-
oxo-1.2,1.3,1.4,1.9,2.3,2.5,2.6,3.7,3.8,4.5,4.9,=
4.10,5.6,5.10,6.7,6.11,7.8,7.11,8.9,8.12,9.12,=
10.11,10.12,11.12-tetracosa-μ-oxo-
dodecakis(oxotungstate)(6−)

The polytungstate X has the same formula $[H_2W_{12}=O_{40}]^{6-}$ but one W_3O_{13} group has been turned by 60°.[36] The name is

dihydrogen-1.4.9,2.5.6,3.7.8,10.11.12-tetra-μ_3-
oxo-1.2,1.3,1.4,1.9,2.3,2.5,2.6,3.7,3.8,4.5,4.9,=
4.10,5.6,5.11,6.7,6.11,7.8,7.12,8.9,8.12,9.10,=
10.11,10.12,11.12-tetracosa-μ-oxo-
dodecakis(oxotungstate)(6−)

Note that the polytungstate Y is a decatungstate $[W_{10}O_{32}]^{4-}$ deriving from the Lindqvist structure. Two W_5O_{18} units share four oxygen atoms. This shows the confusion which may arise from trivial nomenclature for somebody who is not very aware of the chemistry of polyoxometalate chemistry, although trivial names are of course more convenient because they are shorter and apparently simpler.

IV.2. Reduced Compounds

Reduction may be treated as shown earlier. The first example to be discussed will be $[H_2W_{12}O_{40}]^{12-}$. It has been shown that the six electrons are localized in a group W_3O_{13} so that those three tungsten atoms are W^{IV}.[37] It has to be noted that the priority for numbering is first given to the metal skeleton and then to the nature of the constituting atoms so that the numbering does not change with respect to the nonreduced Keggin structure. The name will be

dihydrogen-1.4.9,2.5.6,3.7.8,10.11.12-tetra-
μ_3-oxo-1.2,1.3,1.4,1.9,2.3,2.5,2.6,3.7,3.8,=
4.5,4.9,4.10,5.6,5.10,6.7,6.11,7.11,8.9,=
8.12,9.12,10.11,10.12,11.12-tetracosa-μ-oxo-
dodecaoxo[10,11,12-tritungsten(IV)=
nonatungsten(VI)]ate(12−)

In the case of metal-substituted compounds, the reduction may deal with one kind of central atoms only, the most reducible. For instance $[SiMo_2W_{10}O_{40}]^{4-}$ may be reduced by two electrons which are localized on molybdenum atoms, then molybdenum(V), yielding $[SiMo^V_2W_{10}O_{40}]^{6-}$. The name is straightforwardly written down under a shortened form:

tetracosa-μ-oxo-dodecaoxo-μ_{12}-tetraoxosilicato-
O,O',O'',O'''-[dimolybdenum(V)decatungsten](6−)

A more detailed name would require the knowledge of molybdenum(V) localization in the structure.

IV.3. Mixed-Metal Heteropolyanions

There is nothing different with respect to what has been said earlier about isopolyanions. However the number of isomers due to substitution is larger. They can be distinguished using the described above numbering system of metal atoms. In every case, the structure is numbered considering the position of the various metal species in Table 2, giving the lowest locant to the atom coming first.

For instance, a C_{3v} structure in which one tungsten atom has been substituted by one molybdenum atom is named (compound 2, β isomer)[38]

1.2,1.3,1.4,1.9,2.3,2.5,2.6,3.7,3.8,4.5,4.9,4.10,=
5.6,5.11,6.7,6.11,7.8,7.12,8.9,8.12,9.10,10.11,=
10.12,11.12-tetracosa-μ-oxo-dodecaoxo-μ_{12}-
(tetraoxosilicato-$O^{1.4.9},O^{2.5.6},O^{3.7.8},O^{10.11.12}$)-
(1-molybdenumundecatungsten)ate(4−)

If now one $Ti(C_5H_5)^{3+}$ has substituted one tungsten atom in a Keggin structure, the name is

12-cyclopentadienyl-1.2,1.3,1.4,1.9,2.3,2.5,2.6,=
3.7,3.8,4.5,4.9,4.10,5.6,5.10,6.7,6.11,7.8,7.11,=
8.9,8.12,9.12,10.11,10.12,11.12-tetracosa-μ-oxo-
undecaoxo-μ_{12}-(tetraoxosilicato-
$O^{1.4.9},O^{2.5.6},O^{3.7.8},O^{10.11.12}$)-(12-titanium=
undecatungsten)ate(5−)

The 12 tungsten atoms of the Keggin structure are equivalent. This is no longer true if one considers that a one M_3O_{13} group has turned by 60°. There are three skeletal plane, in which one atom may be substituted, leading to three isomers which are trivially called $\beta 1$, $\beta 2$, and $\beta 3$. Let us take the examples of $[SiVW_{11}O_{40}]^{5-}$ and let us give the three names in this order. The hierarchy of rules requires to start with the overall symmetry and then the application of Table 2 is taken into account. We thus have three different numbers for vanadium in those three compounds.

compound trivially called $\beta 1$

1.2,1.3,1.4,1.9,2.3,2.5,2.6,3.7,3.8,4.5,4.9,4.10,=
5.6,5.11,6.7,6.11,7.8,7.12,8.9,8.12,9.10,10.11,=
10.12,11.12-tetracosa-μ-oxo-dodecaoxo-μ_{12}-
(tetraoxosilicato-$O^{1.4.9},O^{2.5.6},O^{3.7.8},O^{10.11.12}$)-
(undecatungsten-3-vanadium)ate(5−)

compound trivially called $\beta 2$

1.2,1.3,1.4,1.9,2.3,2.5,2.6,3.7,3.8,4.5,4.9,4.10,=
5.6,5.11,6.7,6.11,7.8,7.12,8.9,8.12,9.10,10.11,=
10.12,11.12-tetracosa-μ-oxo-dodecaoxo-μ_{12}-
(tetraoxosilicato-$O^{1.4.9},O^{2.5.6},O^{3.7.8},O^{10.11.12}$)-
(undecatungsten-9-vanadium)ate(5−)

compound trivially called $\beta 3$

1.2,1.3,1.4,1.9,2.3,2.5,2.6,3.7,3.8,4.5,4.9,4.10,=
5.6,5.11,6.7,6.11,7.8,7.12,8.9,8.12,9.10,10.11,=
10.12,11.12-tetracosa-μ-oxo-dodecaoxo-μ_{12}-
(tetraoxosilicato-$O^{1.4.9},O^{2.5.6},O^{3.7.8},O^{10.11.12}$)-
(undecatungsten-12-vanadium)ate(5−)

This numbering system provides a key to name compounds with a larger number of substituted atoms. Let us assume a compound having the Keggin structure and containing two molybdenum atoms and one vanadium atom. The lowest locant, i.e., 1, is given to molybdenum and then the highest possible to vanadium, depending on its location in the metal framework.

One of the various isomers of $[SiMo_2VW_9O_{40}]^{5-}$ is named

1.2,1.3,1.4,1.9,2.3,2.5,2.6,3.7,3.8,4.5,4.9,4.10,=
5.6,5.10,6.7,6.11,7.8,7.11,8.9,8.12,9.12,10.11,=
10.12,11.12-tetracosa-μ-oxo-dodecaoxo-μ_{12}-
(tetraoxosilicato-$O^{1.4.9},O^{2.5.6},O^{3.7.8},O^{10.11.12}$)-
[1,2-dimolybdenum(VI)nonatungsten(VI)-3-
vanadium(V)]ate(5−)

This system can be applied to much more complicated structures. Let us take the example of $[As^{III}_2As^VMo_8V_4O_{40}]^{5-}$.[20] This species contains a central As^VO_4 ligand and two outer $As^{III}O_4$ ligands (Figure 22). The name is
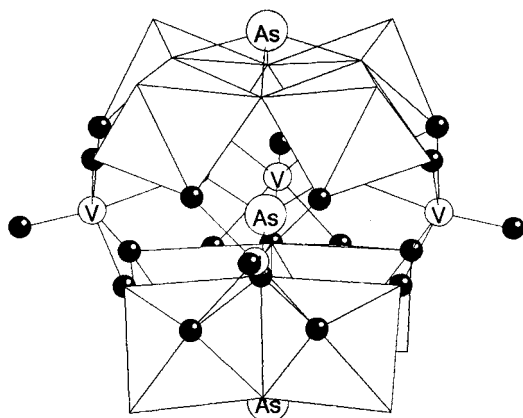
Figure 22. $[As^{III}_2As^VMo_8V_4O_{40}]^{5-}$. Molybdenum atoms are octahedrally surrounded. Black circles are oxygen atoms surrounding either arsenic or vanadium atoms the symbols of which are written inside open circles.

hexadecaoxo[tetraoxoarsenato(3−)]bis=
[tetraoxoarsenato(5−)][octakis(oxomolybdenum)=
tetrakis(oxovanadium)]ate(5−)

Tetraoxoarsenate(5−) immediately points out a very peculiar feature. It contains arsenic(III), therefore there is a lone pair, but four oxygen atoms bound to arsenic, which means that the group is square pyramidal with arsenic at the top of the pyramid. Some space has to be given to the lone pair.

All the structural details are not included in such a name and it is not possible to rebuild the structure from the name. A more detailed name would be much easier to handle for such a purpose. There is a price to pay; the length of the name will increase. The κ convention gives all the details about the connection between every oxygen atom and every metal atom. The numbering of metal atoms has to be carried out, applying rules stated earlier. The axis of symmetry is perpendicular to three metal atom planes, two external skeletal plane containing four molybdenum atoms, and one internal skeletal plane containing four vanadium atoms. One then finds in sequence the following numbering: Mo 1, Mo 2, Mo 3, Mo 4, V 5, V 6, V 7, V 8, Mo 9, Mo 10, Mo 11, Mo 12. Each molybdenum atom is connected to two vanadium atoms by an oxo bridge, and each vanadium atom is connected to two molybdenum atoms by an oxo bridge.

The name becomes

1.5,1.8,2.5,2.6,3.6,3.7,4.7,4.8,5.9,5.10,6.10,=
6.11,7.11,7.12,8.9,8.12-hexadeca-μ-oxo-μ_{12}-
[tetraoxoarsenato(V)]-
1:4:8κO;2:3:6$\kappa O'$,5:9:10$\kappa O''$,7:11:12$\kappa O'''$-
bis[μ_4-tetraoxoarsenato(III)]-
1:2κO;1:4$\kappa O'$,2:3$\kappa O''$,3.4$\kappa O'''$;9:10κO;9:12$\kappa O'$,=
10:11$\kappa O''$,11:12$\kappa O''$-[octakis(oxomolybdenum)-
5,6,7,8-tetrakis(oxovanadium)]ate(5−)

This name has been discussed in details in order to show how the system may be applied.

IV.4. Compounds with One Vacant Metal Site

One metal atom may be missing yielding an 11 metal atom polyoxotungstate, $[SiW_{11}O_{39}]^{8-}$. One WO group has been "taken away". This may happen either for the α-isomer or isomer 1 as referred above,

or for the β-isomer or isomer 2. In the first case, the 12 positions of the dodecatungstate are equivalent and there is only one possibility to withdraw one tungsten atom. In the second case, there are three possibilities, depending on the location of the missing tungsten atom, in the turned M_3O_{13} group, in the internal skeletal plane of six tungsten atoms attached to this group, or in the less condensed three tungsten atom terminal skeletal plane opposed to the turned M_3O_{13} group.

The rules stated in section II.2 require that the numbering starts from the preferred skeletal plane which has first the fewest number of central atoms and second the less condensed situtation. An 11 tungsten polytungstate has no symmetry axes but skeletal planes and the preferred terminal skeletal plane contains only two tungsten atoms and the unoccupied position.

In the four preceding cases, the short name will be the same:

icosa-μ-oxo-μ_{11}-tetraoxosilicato-
pentadecaoxoundecatungstate(8−)

To distinguish between isomers, a more detailed name is needed. It implies numbering of tungsten atoms which must start from the preferred terminal skeletal plane. The determination of the 12 o'clock position requires that the numbering has to be worked out in each case. By example, for the compound derived from the Keggin structure, $[SiW_{11}O_{39}]^{8-}$, one gets the following name:

1.2,1.3,1.4,2.7,2.8,3.4,3.8,3.9,4.5,4.10,5.6,=
5.10,6.7,6.11,7.8,7.11,8.9,9.10,9.11,10.11-
icosa-μ-oxo-μ_{11}-(tetraoxosilicato-
$O^{1.3.4},O^{2.7.8},O^{5.6},O^{9.10.11}$)-pentadecaoxoundeca=
tungstate(8−)

Let us give two examples for the compound deriving from the dodecatungstate in which one group has turned by 60°, the first example for which the tungsten is taken off from the turned group, the second example for which the withdrawn tungsten atom is chosen among the three atoms opposite to the turned group:

1.2,1.4,1.5,2.6,2.7,3.4,3.8,3.9,4.5,4.10,5.6,5.10,=
6.7,6.11,7.8,7.11,8.9,9.10,9.11,10.11-icosa-μ-
oxo-μ_{11}-(tetraoxosilicato-$O^{1.4.5},O^{2.6.7},O^{3.8},O^{9.10.11}$)-
pentadecaoxoundecatungstate(8−)

and

1.2,1.4,1.5,2.6,2.7,3.4,3.8,3.9,4.5,4.10,5.6,5.10,=
6.7,6.11,7.8,7.11,8.9,9.10,9.11,10.11-icosa-μ-
oxo-μ_{11}-(tetraoxosilicato-$O^{1.2},O^{3.8.9},O^{4.5.10},O^{6.7.11}$)-
pentadecaoxoundecatungstate(8−)

In the last case, which actually is observed experimentally, one can fill the vacancy with one molybdenum atom.[37] The numbering has to be reconsidered on the basis of a dodecametalate taking into account the rule requiring that molybdenum atom must have number 1 from Table 2 so that the name of the compound becomes

1.2,1.3,1.4,1.9,2.3,2.5,2.6,3.7,3.8,4.5,4.9,4.10,=
5.6,5.11,6.7,6.11,7.8,7.12,8.9,8.12,9.10,10.11,=
10.12,11.12-tetracosa-μ-oxo-μ_{12}-(tetraoxosilicato-
$O^{1.4.9},O^{2.5.6},O^{3.7.8},O^{10.11.12}$)-dodecaoxo(1-
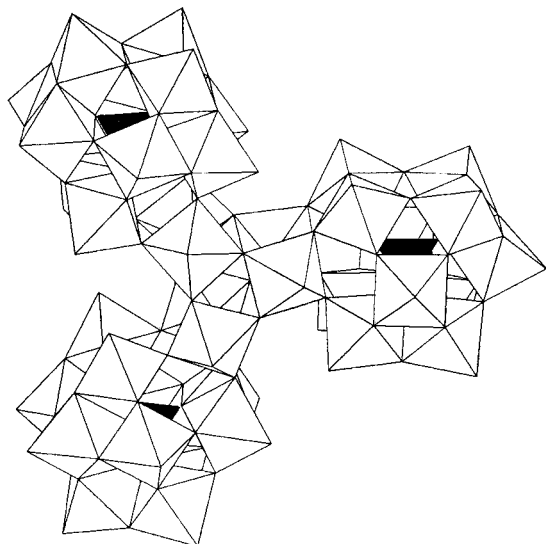molybdenumundecatungsten)ate(4−)

Figure 23. Drawing of $[B_3W_{39}O_{132}]^{21-}$. The three black tetrahedrons contain boron atoms.

The lacunar compound $[PW_{11}O_{39}]^{8-}$ directly derived from the Keggin structure may be used as a ligand bound to a dirhodium core.[38] The name is straightforwardly deduced from this given above and used as such with the ending -o to express that it is a ligand:

di-μ-(acetato-O,O')-bis(dimethyl sulfoxide-S)-μ-[1.2,1.3,1.4,2.7,2.8,3.4,3.8,3.9,4.5,4.10,5.6,= 5.10,6.7,6.11,7.8,7.11,8.9,9.10,9.11,10.11-icosa-μ-oxo-μ_{11}-(tetraoxophosphato-$O^{1.3.4},O^{2.7.8},O^{5.6},O^{9.10.11}$)-pentadecaoxoundeca= tungstato(8−)-O^{1c},O^{5d}:O^{2b},O^{6e}]-dirhodate(5−)= ($Rh-Rh$)

Rh−Rh with a long hyphen means that there is a rhodium−rhodium bond. O^{1c},O^{5d}:O^{2b},O^{6e} indicates that the oxygen atoms O^{1c} and O^{5d} are bound to the first rhodium atoms, and that O^{2b} and O^{6e} atoms are bound to the second rhodium atom.

Very few examples of boron-containing polyoxotungstates are known. $[B_3W_{39}O_{132}]^{21-}$ is one of those.[39] It is a symmetrical compound which contains three BW_{11} units arranged around a W_6O_{27} group so that the whole compound has a ternary axis of symmetry (Figure 23). It seems better to treat this central core of six octahedrally surrounded tungsten atoms as a bridge connecting the three undecatungstate units which derive from a Keggin structure. Thus a name has first to be given to that bridge.

The bridge is made of two rings of three octahedrons sharing three corners. The two rings are one above the other and they share three oxygen atoms so that the six tungsten atoms build a trigonal prismatic framework, the numbering of which is 1,2,3 for the upper ring and 4,5,6 for the lower ring. Each octahedron of the bridge is connected to two tungsten atoms of one undecatungstate, so that the hexatungsten bridge is μ_{12}:

μ_{12}-{1.4,2.5,3.6-tri-μ-oxo-[$cyclo$-1.2,1.3,2.3-tri-μ-oxo-tris(trioxotungstato)][$cyclo$-4.5,4.6,5.6-tri-μ-oxo-tris(trioxotungstato)]-1κO^1,2κO^4,5$\kappa O^{1'}$,= 6$\kappa O^{4'}$;1'κO^2,2'κO^5,5'$\kappa O^{2'}$,6'$\kappa O^{5'}$;1''κO^3,2''κO^6,= 5''$\kappa O^{3'}$,6''$\kappa O^{6'}$}-tris[1.2,1.3,1.4,2.7,2.8,3.4,3.8,= 3.9,4.5,4.10,5.6,5.10,6.7,6.11,7.8,7.11,8.9,=

9.10,9.11,10.11-icosa-μ-oxo-μ_{11}-(tetraoxoborato-$O^{1.3.4},O^{2.7.8},O^{5.6},O^{9.10.11}$)-undecakis(oxo= tungstate)](21−)

The sequence 1κO^1,2κO^4,5$\kappa O^{1'}$,6$\kappa O^{4'}$ indicates that an oxygen atom fixed on tungsten 1 of the ligand is ligated to tungsten 1 of a first undecatungstate, an oxygen fixed on tungsten 4 of the ligand is ligated to tungsten 2 of the same undecatungstate, another oxygen fixed on tungsten 1 of the ligand is ligated to tungsten 5 of the same undecatungstate, and another oxygen fixed on tungsten 4 of the ligand is ligated to tungsten 6 of the same undecatungstate, and so on.

IV.5. Compounds with Three Vacant Metal Sites

The nine metal atom polyoxometalates derived from the Keggin structure give rise to a large variety of compounds. First of all, one has to consider the nine metal atom entity as a free group, regardless of its existence or not, because it may be used as a building block for the synthesis of other compounds.

Three metal atoms belonging to the same skeletal plane may be taken off the Keggin structure. However they may be taken either from the upper skeletal plane, i.e., from one M_3O_{13} group, or from the lower skeletal plane, i.e., from three different M_3O_{13} groups (Figure 24). The first case occurs with an heteroatom such as P^V or As^V, because their four surrounding oxygen atoms are still connected to metal atoms. The second case occurs with an heteroatom such as As^{III} or Sb^{III} because the lone pair needs some free space.

The first case is trivially called type A. An example is $[PMo_9O_{28}(OH)_6]^{3-}$, the name of which is (compound III) (Figure 25):[40]
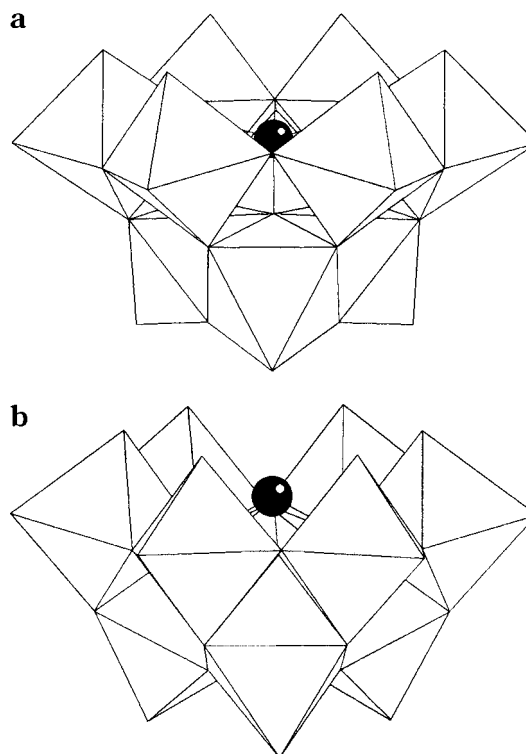

Figure 24. Nine metal atom polyoxometalates. Part a is known as type A, it contains a X^{IV} or X^V heterotatom. Part b is known as type B, it contains a X^{III} heteroatom which has a free lone pair. The X heteroatom is shown as a black circle.
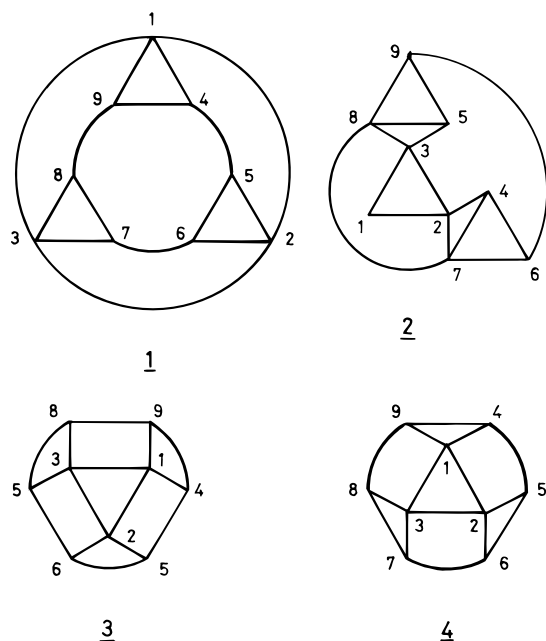
Figure 25. Nine atom polyoxometalates. It shows only metal centers with their numbering. Isomer 1 is a Keggin structure which has lost a M_3O_{13} group. Isomer 2 is the preceding isomer with one group M_3O_{13} group turned. Isomer 3 is a Keggin structure which has lost three metal atoms taken in three different M_3O_{13} groups. Isomer 4 is the Keggin isomer 2 which has lost three metal atoms taken in the three different unturned M_3O_{13} groups. A circle line means a common corner between the two related octahedrons.

4f,5f,6f,7f,8f,9f-hexahydroxo-1c.2a,1a.3c,1f.4a,=
1e.9a,2c.3a,2e.5a,2f.6a,3e.7a,3f.8a,4c.5b,4d.9e,=
5e.6d,6c.7b,7e.8d,8c.9b-pentadeca-μ-oxo-μ_9-
[tetraoxophosphato(V)-$O^{1.2.3},O^{4.5},O^{6.7},O^{8.9}$]-
nonakis(oxomolybdate)(3−)

This name points out the location of the six OH groups which occupy the six uppermost pending octahedron vertices.

The second case is trivially known as type B. $[As^{III}W_9O_{33}]^{9-}$ is named (compound I):[41]

1c.2b,1b.3c,1e.4a,1d.9a,2c.3b,2d.5a,2e.6a,=
3d.7a,3e.8a,4c.5d,4d.9e,5e.6d,6c.7b,7e.8d,=
8c.9b-pentadeca-μ-oxo-pentadecaoxo-μ_9-
[trioxoarsenato(III)-$O^{1.4.9},O^{2.5.6},O^{3.7.8}$]-
nonatungstate)(9−)

One may see that μ-oxo bridges have the same numerical locants but they differ when literal locants are added; the numbering of the μ_9 bridge is also different.

As it happens for the Keggin structure, one may turn one M_3O_{13} group by 60°, which yields isomers trivially designated as Aβ and Bβ while the preceding ones are Aα and Bα. They are systematically named as

$[SiW_9O_{34}]^{10-}$ with a group turned by 60° (compound IV)

1c.2a,1a.3c,1f.4a,1e.9a,2c.3a,2e.5a,2f.6a,3e.7a,=
3f.8a,4e.5d,4b.9c,5c.6b,6e.7d,7c.8b,8e.9d-
pentadeca-μ-oxo-pentadecaoxo-μ_9-
[tetraoxosilicato-$O^{1.2.3},O^{4.9},O^{5.6},O^{7.8}$]-
nonatungstate)(10−)

$[As^{III}W_9O_{33}]^{9-}$ with a group turned by 60° (compound II)

1c.2a,1d.3a,2d.3c,2b.4b,2f.7b,3e.5a,3f.8a,4e.6c,=
4f.7c,5e.8c,5f.9c,6f.7e,6d.9d,7d.8d,8f.9e-
pentadeca-μ-oxo-pentadecaoxo-μ_9-
[trioxoarsenato(III)-$O^{1.2.3},O^{4.6.7},O^{5.8.9}$]-
nonatungstate)(9−)

To close this part, let us note that all these units look like a basket.

IV.6. Three Vacant Metal Site Heteropolyanions with Mixed Ligands

The open side of the basket may be used to bind some other organic or inorganic ligands.

For instance, twice two uppermost oxygen atoms of the basket belonging to two octahedrons sharing an edge may be substituted by a phosphonate μ-$C_2H_5PO_3^{2-}$, yielding $[P^VW_9O_{30}(C_2H_5PO_3)_2]^{6-}$ (Figure 26).[42] The nonatungstate PW_9O_{34} is derived from the Keggin structure (compound 1, type Aα). It is named

bis[μ-(ethylphosphonato-O,O')]-pentadeca-μ-
oxo-dioxo-μ_9-[tetraoxophosphato(V)]-
nonakis(oxomolybdate)(6−)

or to be more accurately

bis(μ-ethylphosphonato)-$O^6,O^7;O^8,O^9$-
1.2,1.3,1.4,1.9,2.3,2.5,2.6,3.7,3.8,4.5,4.9,5.6,=
6.7,7.8,8.9-pentadeca-μ-oxo-4,5-dioxo-μ_9-
[tetraoxophosphato(V)-$O^{1.2.3},O^{4.5},O^{6.7},O^{8.9}$]-
nonakis(oxotungstate)(6−)

4,5-Dioxo is so numbered because O has priority over $C_2H_5PO_3^{2-}$. $^tBuSiO_2(OH)^{2-}$ or $(C_6H_5)_2SiO_2^{2-}$ behave the same way and names may be derived similarly.[42]

The same type of compound may be prepared with a tripod-shaped ligand $C_2H_5Si[OSi(C_2H_5)O_2]_3^{6-}$. Each diolate is bound to two tungsten atoms as above and the nonatungstate is the same (Figure 27), the formula is $[P^VW_9O_{28}\{C_2H_5Si[OSi(C_2H_5)O_2]_3\}]^{3-}$.[43]

μ_6-ethylsilanetris[oxy(ethyl)silanediolato]-
$4\kappa O^1,5\kappa O^{1'},6\kappa O^2,7\kappa O^{2'},8\kappa O^3,9\kappa O^{3'}$-1.2,1.3,1.4,1.9,=
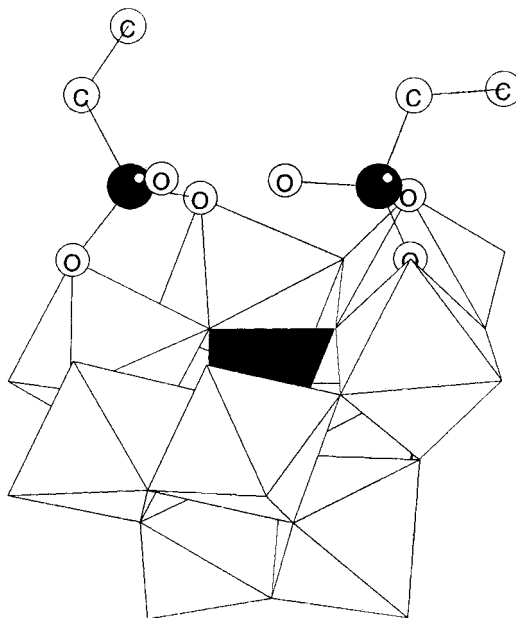

Figure 26. Two phosphonate ligands share the uppermost oxygen atoms of PW_9O_{34}, yielding $[P^VW_9O_{30}(C_2H_5PO_3)_2]^{5-}$. The phosphorus(V)-containing central tetrahedron is black. Symbols of oxygen and carbon atoms are written inside open circles. Black circles are phosphorus atoms.
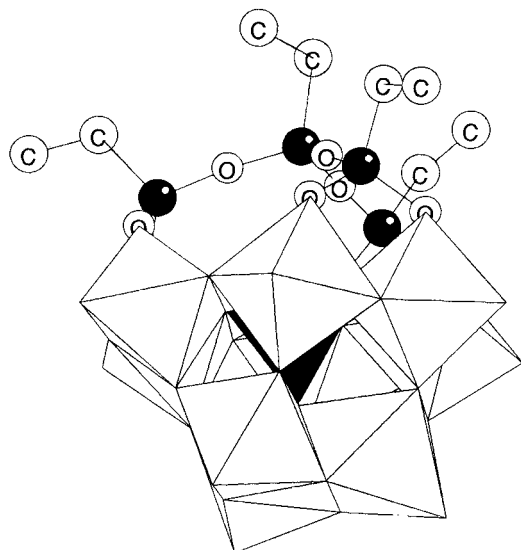
Figure 27. $[P^VW_9O_{28}\{C_2H_5Si[OSi(C_2H_5)O_2]_3\}]^{3-}$. The phosphorus(V)-containing central tetrahedron is black. Symbols of oxygen and carbon atoms are written inside open circles. Black circles are silicon atom.
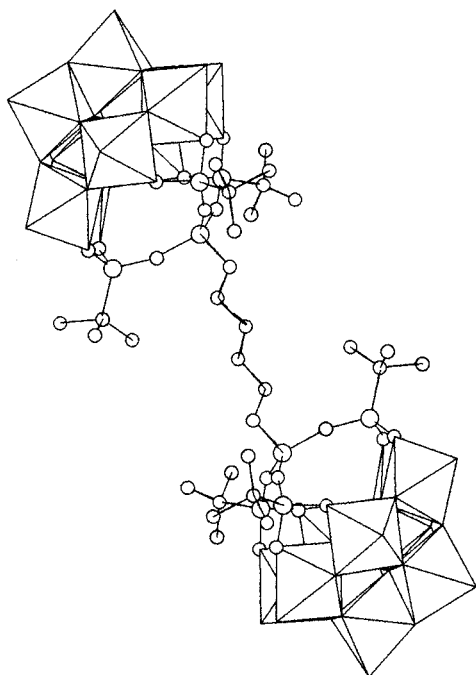
Figure28. $[P^VW_9O_{28}\{[O_2Si(C_2H_5)O]_3Si(CH_2)_6Si[OSi(C_2H_5){=}O_2]_3\}P^VW_9O_{28}]^{6-}$. Two nonatungstates are connected by a bridging symmetrical hexakis(diol).

2.3,2.5,2.6,3.7,3.8,4.5,4.9,5.6,6.7,7.8,8.9-
pentadeca-μ-oxo-μ_9-[tetraoxophosphato(V)-
$O^{1.2.3},O^{4.5},O^{6.7},O^{8.9}$]-nonakis(oxotungstate)(3−)
$4\kappa O^1,5\kappa O^{1'}$ shows that the two olato groups ligated to tungsten 4 and 5 come from the same $Si(C_2H_5)O_2$ group.

Two nonatungstates may be bridged by using a symmetrical ligand $[O_2(C_2H_5)SiO]_3Si(CH_2)_6Si[OSi{=}(C_2H_5)O_2]_3^{12-}$. It contains two three disilanolate ligating groups, one at each end of the molecule; therefore, one gets $[P^VW_9O_{28}\{[O_2Si(C_2H_5)O]_3Si{=}(CH_2)_6Si[OSi(C_2H_5)O_2]_3\}P^VW_9O_{28}]^{3-}$ (Figure 28):[42]

μ_{12}-hex-1,6-diylbis{silanetris[oxy(ethyl)silane=
diolato]}-$4\kappa O^1,5\kappa O^{1'},6\kappa O^2,7\kappa O^{2'},8\kappa O^3,9\kappa O^{3'};{=}$
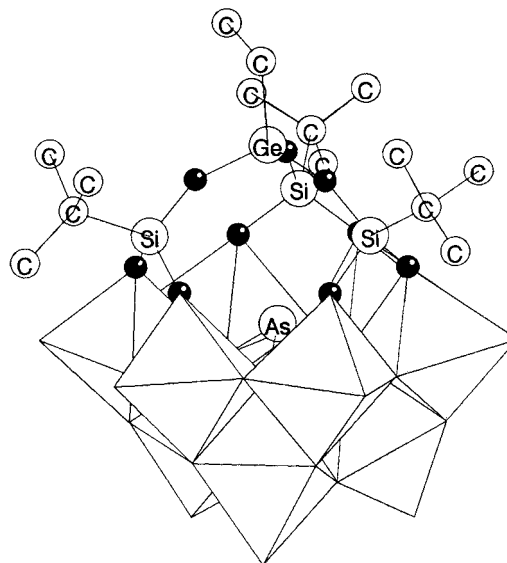
Figure 29. $[As^{III}W_9O_{27}\{C_2H_5Ge[OSi(^tBu)O_2]_3\}]^{3-}$, this compound differs from this of Figure 27; it is based on an arsenic(III)-containing nonatungstate instead of a phosphorus(V)-containing nonatungstate, i.e. isomer 1 (type B) instead of isomer 3 (type A). Symbols of arsenic, carbon, germanium, and silicon atoms are written inside open circles. Black circles are oxygen atoms of the $C_2H_5Ge[OSi(^tBu)O_2]_3$ group.

$4'\kappa O^1,5'\kappa O^{1'},6'\kappa O^2,7'\kappa O^{2'},8'\kappa O^3,9'\kappa O^{3'}$-
bis{1.2,1.3,1.4,1.9,2.3,2.5,2.6,3.7,3.8,4.5,4.9,=
5.6,6.7,7.8,8.9-pentadeca-μ-oxo-[tetraoxo=
phosphato(V)-$O^{1.2.3},O^{4.5},O^{6.7},O^{8.9}$]-nonakis=
(oxotungstate)}(3−)

Another compound using the same type of ligand has been prepared with an arsenic(III) containing nonatungstate deriving from the Keggin structure by the loss of a M_3O_{13} group (compound 2, type Bα), $[As^{III}W_9O_{27}\{C_2H_5Ge[OSi(C_2H_5)O_2]_3\}]^{3-}$.[42] In that case the ligation of the organometallic anion is different (Figure 29). Each silanediolate is ligated to two tungsten atoms belonging to two octahedrons sharing only one corner; this is shown by the sequence of locants following the ligand name:

μ_6-ethylgermanetris[oxy(tertiobutyl)silanediolato]-
$4\kappa O^1,5\kappa O^2,6\kappa O^{2'},7\kappa O^3,8\kappa O^{3'},9\kappa O^{1'}$-1.2,1.3,1.4,1.9,=
2.3,2.5,2.6,3.7,3.8,4.5,4.9,5.6,6.7,7.8,8.9-
pentadeca-μ-oxo-μ_9-[trioxoarsenato(III)-
$O^{1.4.9},O^{2.5.6},O^{3.7.8}$]-nonakis(oxotungstate)(3−)

IV.7. Higher Nuclearity Species Based on Nine Tungsten Atom Fragments

$[H_2AsW_{18}O_{60}]^{7-}$ is made of two nine tungsten atom units, one containing an arsenic(III) atom, i.e., AsW_9O_{33}, the other containing two hydrogen atoms, i.e., $H_2W_9O_{33}$.[44] They both derive from a Keggin structure of which a W_3O_{13} group has been taken away (compound 2, type Bα). Those two units share six oxygen atoms. The same type of compound occurs with antimony that is $[H_2SbW_{18}O_{60}]^{7-}$.[45] However these two compounds differ because the tungsten framework has a center of symmetry in the case of the arsenic-containing compound while this framework has a plane of symmetry in the case of the antimony-containing compound (Figure 30).
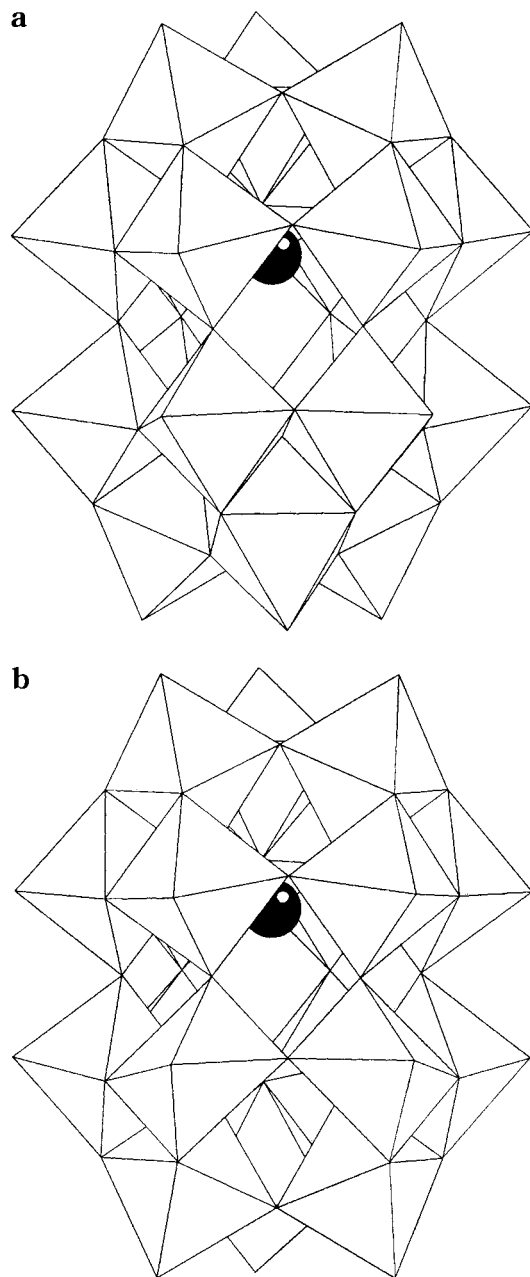
a

b

Figure 30. Comparison of $[H_2As^{III}W_{18}O_{60}]^{7-}$ (a) and $[H_2Sb^{III}W_{18}O_{60}]^{7-}$ (b) showing the center of symmetry for a and the plane of symmetry for b. The heteroatom, As or Sb, is shown as a black circle.

Simple names such as

dihydrogen(trioxoarsenato)heptapentaconta=
octadecatungstate(7−)

and

dihydrogen(trioxostibato)heptapentaconta=
octadecatungstate(7−)

do not reflect this difference of symmetry, nor it shows where the heteroatom is and where the hydrogen atoms are. This can be achieved by numbering the tungsten skeleton. Thus the two names will be

1.4.9,2.5.6-di-μ_3-hydroxo-3.7.8-μ_3-oxo-
1.2,1.3,1.4,1.9,2.3,2.5,2.6,3.7,3.8,4.5,4.9,4.10,=
5.6,5.11,6.7,6.12,7.8,7.13,8.9,8.14,9.15,10.11,=
10.15,10.16,11.12,11.16,12.13,12.17,13.14,=
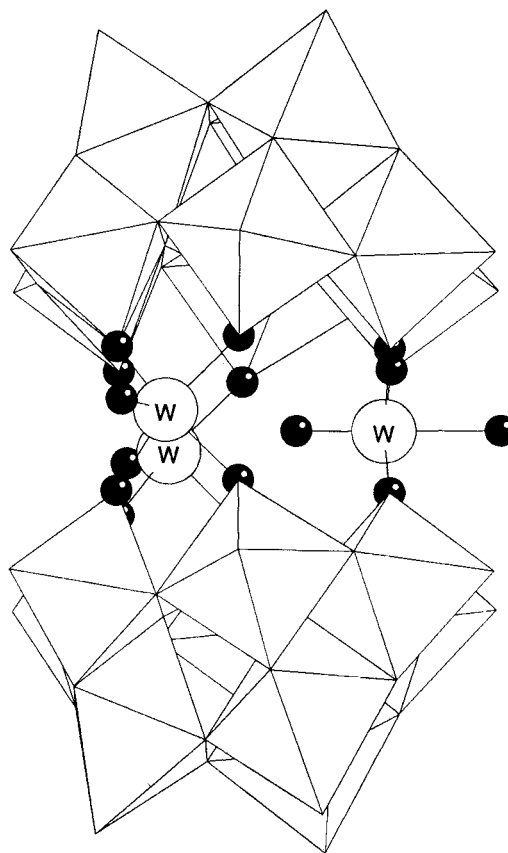13.17,14.15,14.18,15.18,16.17,16.18,17.18-

Figure 31. $[As^{III}_2W_{21}O_{69}(H_2O)]^{6-}$ is made of two As^{III}-containing nonatungstates (isomer 1) joined by one octahedron $WO_5(H_2O)$ and two square pyramids WO_5. Black circles are oxygen atoms of the connecting $WO_5(H_2O)$ octahedron and both WO_5 square pyramids. The water molecule is at the right of the figure.

hexatriaconta-μ-oxo-μ_9-[trioxoarsenato(III)-
$O^{10.11.16}, O^{12.13.17}, O^{14.15.18}$]-octadecakis=
(oxotungstate)(7−)

and

1.4.9,2.5.6-di-μ_3-hydroxo-3.7.8-μ_3-oxo-
1.2,1.3,1.4,1.9,2.3,2.5,2.6,3.7,3.8,4.5,4.9,=
4.10,5.6,5.11,6.7,6.12,7.8,7.13,8.9,8.14,9.15,=
10.11,10.15,10.16,11.12,11.16,12.13,12.17,=
13.14,13.17,14.15,14.18,15.18,16.17,16.18,=
17.18-hexatriaconta-μ-oxo-μ_9-[trioxostibato=
(III)-$O^{10.15.16}, O^{11.12.17}, O^{13.14.18}$]-octadecakis=
(oxotungstate)(7−)

It can be seen that the two compounds are distinguished by the locants assigned to the ligating atoms of AsO_3 or SbO_3 groups.

Another tungsten compound $[H_2As_2W_{21}O_{70}]^{6-}$ contains two $As^{III}W_9O_{33}$ units (compound 2, type Bα) connected by three tungsten-containing polyhedrons, two square pyramids WO_5, and one octahedron $WO_5(H_2O)$ (Figure 31).[46] Each of these joints share four basal plane oxygen atoms, two with the upper W_9 unit, two with the lower W_9 unit. In such a case, because both AsW_9O_{33} units are identical, the three connecting polyhedrons will be treated as ligands to make the name simpler.

μ_4-(aquapentaoxotungstato-$O,O':O'',O'''$)-
bis[μ_4-(pentaoxotungstato-$O,O':O'',O'''$)-
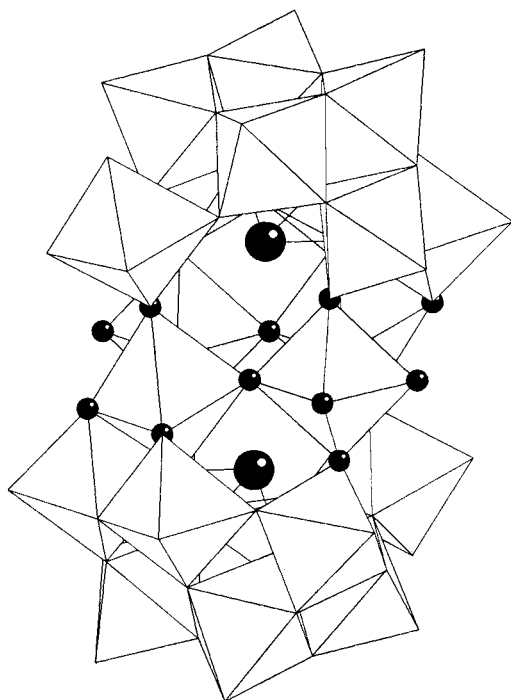bis[pentadeca-μ-oxo-μ_9-trioxoarsenato(III)-
nonakis(oxotungstate)](6−)

Figure 32. $[H_2Sb^{III}_2W_{22}O_{76}]^{12-}$ is made of two Sb^{III}-containing nonatungstates in which one W_3O_{13} group has turned (isomer 2). They are joined by four octahedrons which are shown by their surrounding oxygen atoms represented by small black circles. Antimony atoms are large black circles.

A more elaborate name describing the accurate location of all the oxygen atoms in order to be able to reconstruct the structure is

μ_4-aquapentaoxotungstato-
$4\kappa O,5\kappa O',4'\kappa O'',5'\kappa O'''$-bis[$\mu_4$-(pentaoxo=
tungstato)]-$6\kappa O,7\kappa O',6'\kappa O'',7'\kappa O''$:$8\kappa O,9\kappa O,=$
$8'\kappa O'',9'\kappa O'''$-bis{1.2,1.3,1.4,1.9,2.3,2.5,2.6,3.7,=
3.8,4.5,4.9,5.6,6.7,7.8,8.9-pentadeca-μ-oxo-μ_9-
[trioxoarsenato(III)-$O^{1.4.9},O^{2.5.6},O^{3.8.9}$]-
nonakis(oxotungstate)}(6−)

The numbering of each W_9 unit is the same because they are structurally identical and consequently numbered independently; hence, bis is put in front of the W_9 unit name. However to distinguish the ligated sites of the first and of the second unit, 4 and 4′ have been used, 4 for W_9 unit number one and 4′ for unit number two.

The nonatungstate unit $Sb^{III}W_9O_{33}$ is found into the $[H_2Sb^{III}_2W_{22}O_{76}]^{12-}$ polytungstate (Figure 32).[45,55] It may described as two $Sb^{III}W_9O_{33}$ groups in which one W_3O_{13} group has turned by 60°, i.e., it corresponds to compound 4, type Bβ. The W_9 skeleton has lost its C_3 axis of symmetry but the numbering remains possible following rules stated in section II.2 and using the geometry deduced from an X-ray diffraction study. Note that the numbering is different than what has been given above because the observed geometry does not correspond to the geometry assumed above. Both $Sb^{III}W_9O_{33}$ units are bound by four octahedrons, two WO_6 and two $WO_5(OH)$ octahedrons. A locant assignment of the W_9 units is necessary to make clear the way those octahedrons bridge the units.

bis(μ_4-hexaoxotungstato)-
$O^1,O^2,O^{2'},O^{3'};O^2,O^3,O^{1'},O^{2'}$-bis($\mu_3$-hydroxopenta=
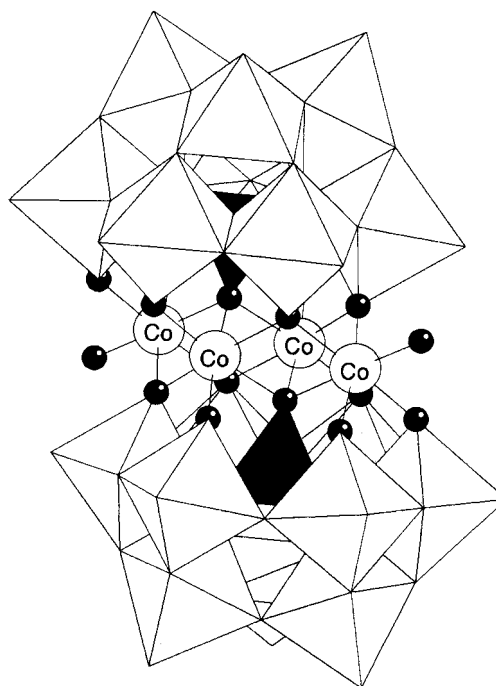
Figure 33. $[Co_4(As^VW_9O_{34})_2(H_2O)_2]^{10-}$; a core of four fused cobalt-containing octahedrons is ligated to two $As^VW_9O_{34}$ units (isomer 3) ligated each by one oxygen atom of As^VO_4 and by six oxygen atoms of the nonatungstate unit. Both arsenic containing tetrahedrons are black. Cobalt atoms are shown as open circles with the Co symbol inside and oxygen atoms octahedrally surrounding cobalt atoms are black.

oxotungstato)-$O^5,O^6,O^{1'};O^1,O^{5'},O^{6'}$-
bis{1.4,1.7,2.4,2.5,2.8,3.6,3.7,3.9,4.7,4.8,5.6,=
5.8,6.9,7.9,8.9-pentadeca-μ-oxo-2,3,4,5,6,7,8,9-
octaoxo-μ_9-[trioxostibato(III)-$O^{1.4.7},O^{2.5.8},O^{3.6.9}$]-
nonatungstate}(12−)

The ligand name bis(μ_4-hexaoxotungstato-$O^1,O^2,O^{2'},O^{3'}$; $O^2,O^3,O^{1'},O^{2'}$) means that a first bridging WO_6 octahedron is bound to tungsten atoms number 1 and 2 of the first SbW_9 unit and to tungsten number 2 and 3 of the second SbW_9 and that the second bridging WO_6 octahedron is bound to tungsten atoms number 2 and 3 of the first SbW_9 unit and to tungsten atoms number 1 and 2 of the second SbW_9.

A species keeping the same geometry may be prepared by substituting both bridging $WO_5(OH)$ octahedrons by two $Fe^{III}O_3(H_2O)_3$ octahedrons.[45] Then the name becomes

bis(μ_4-hexaoxotungstato)-
$O^1,O^2,O^{2'},O^{3'};O^2,O^3,O^{1'},O^{2'}$-bis($\mu_3$-
triaquatrioxoferrato)-$O^5,O^6,O^{1'};O^1,O^{5'},O^{6'}$-
bis{1.4,1.7,2.4,2.5,2.8,3.6,3.7,3.9,4.7,4.8,5.6,=
5.8,6.9,7.9,8.9-pentadeca-μ-oxo-2,3,4,5,6,7,8,9-
octaoxo-μ_9-[trioxostibato(III)-$O^{1.4.7},O^{2.5.8},O^{3.6.9}$]-
nonatungstate}(8−).

Another more difficult case (Figure 33) is a Keggin structure $[As^VW_{12}O_{40}]^{3-}$ which has lost a group W_3O_{13}, yielding the fragment $[As^VW_9O_{34}]^{9-}$, similar to compound 2, type Bα, with however an arsenic(V) bearing a pending oxygen atom instead of an arsenic-(III) atom. Two such groups are ligated to a group of four cobalt-centered octahedrons sharing edges and making a $Co_4O_{14}(H_2O)_2$ fragment. Seven oxygen atoms are shared between this group and $As^VW_9O_{34}$,

six being ligated to tungsten and one to arsenic. The formula is $[Co_4(As^VW_9O_{34})_2(H_2O)_2]^{10-}$.[47]

A name might be

diaquabis{μ_4-[μ_9-tetraoxoarsenato(V)-pentadeca-μ-oxo-pentadecaoxononatunsgtato(9−)]}-tetracobaltate(10−)

This name is not too complicated but it does not describe that seven oxygen are shared between each polyanion and the four cobalt atoms, which oxygen atoms of the polyanion are shared, how they are organized around the tetracobalt framework, and how the four cobalt atom framework is fused. It is necessary to identify ligated oxygen atoms and to show them up using the κ convention, hence to number on one hand the W$_9$ unit and on the other hand the Co$_4$ unit. Thus two sets of locants run together. When these three units are numbered, the two W$_9$ and the Co$_4$, each one is numbered for itself, that is independent of the two others.

1,3-aquabis[μ_4-(μ_9-tetraoxoarsenato-$O^{1.4.9},O^{2.5.6},O^{3.7.8}$)-1.2.3$\kappa O$;2.3.4$\kappa O$-1.2,1.3,1.4,=1.9,2.3,2.5,2.6,3.7,3.8,4.5,4.9,5.6,6.7,7.8,8.9-pentadeca-μ-oxo-pentadecaoxononatungstato]-1:2κO^{5f},1:4κO^{4f},1κO^{9f},2κO^{6f},3κO^{7f},3κO^{8f};2:3κO^{4f},=3:4κO^{5f},1κO^{7f},1κO^{8f},2κO^{9f},4κO^{7f}}-tetracobaltate(10−)

The long series of locants using the κ convention shows which oxygen atom of nonatungstates is bound to which cobalt atom and consequently how these cobalt atoms are linked together. For instance, locants such as $1.4\kappa O^{4f}$ shows that oxygen atom number 4f of the polytungstate is bound to cobalt atoms number 4 and 4.

IV.8. A Heteropolyanion with an Eight Metal Atom Skeleton

There is a heterooctatungstate derived from the Keggin structure. It contains eight tungsten atoms and two arsenic(III) atoms. The formula is $[As^{III}_2W_8O_{30}(OH)]^{6-}$ (Figure 34).[48] The framework is described as that of the nine tungsten atom, section

IV.5, compound 4, type Bβ, which has lost one tungsten atom from the turned group W$_3$O$_{13}$ group which now is a W$_2$O$_{10}$ group. There still occurs an As^{III}O$_3$ bridging ligand ligated to the eight tungsten atoms. Another arsenic(III) behaves as a ligand As^{III}O$_2$(OH) bridging two tungsten atoms of the two complete W$_3$O$_{13}$ groups. The fragment AsW$_8$ is very much the same as the building block SbW$_9$ of $[H_2Sb^{III}_2W_{22}O_{76}]^{12-}$, one metal atom has been taken away. The name is

μ_8-(trioxoarsenato-$O^{1.3.4},O^{2.5.6},O^{7.8}$)-$\mu$-(hydroxodioxoarsenato-$O^4,O^5$)-1.2,1.3,1.4,1.7,=2.5,2.6,2.8,3.4,3.7,4.5,5.6,6.8,7.8-trideca-μ-oxo-1,2,3,3,4,5,6,6,7,7,8,8-dodecaoxoocta=tungstate(7−)

IV.9. Heteropolyanions with 18 Central Atoms, the Dawson Structure, and Derivatives

Two P^{V}M$_9$O$_{34}$ or As^{V}M$_9$O$_{34}$ units may fuse by sharing six oxygen atoms, yielding an 18 central atom compound. Examples are $[P^V_2W_{18}O_{62}]^{6-}$, $[P^V_2Mo_{18}O_{62}]^{6-}$, $[As^V_2W_{18}O_{62}]^{6-}$, and $[P^V_2Mo_{18}O_{62}]^{6-}$.[49] The constituting unit derives from the Keggin structure by withdrawing three metal atoms from three different M$_3$O$_{13}$ groups (compound 1, type Aα) (Figure 35). This compound is known as the Dawson compound.

Trying to shorten the name as much as possible would consist of treating the compound as made of two identical groups connected by six oxo bridges. Thus the name would be

hexa-μ-oxo-bis[pentadeca-μ-oxo-μ_9-tetraoxophosphato(V)-nonakis(oxotungstate)](6−)

To indicate more details, the numbering of tungsten atoms of the metal framework becomes necessary. The name, simple in principle, but more difficult to read because of the long series of locants, is

1.2,1.3,1.4,1.9,2.3,2.5,2.6,3.7,3.8,4.5,4.9,4.10,=5.6,5.11,6.7,6.12,7.8,7.13,8.9,8.14,9.15,10.11,=

Figure 34. $[As^{III}_2W_8O_{30}(OH)]^{6-}$. This is a fragment of As^{III}W$_9$O$_{33}$ in which a W$_3$O$_{13}$ group turned (isomer 2) and from which one tungsten atom was withdrawn. In addition a As^{III}O$_2$(OH) group is ligated. The oxygen atoms bound to arsenic atoms are shown by black circles. The OH group is the lowest black circle of the figure.
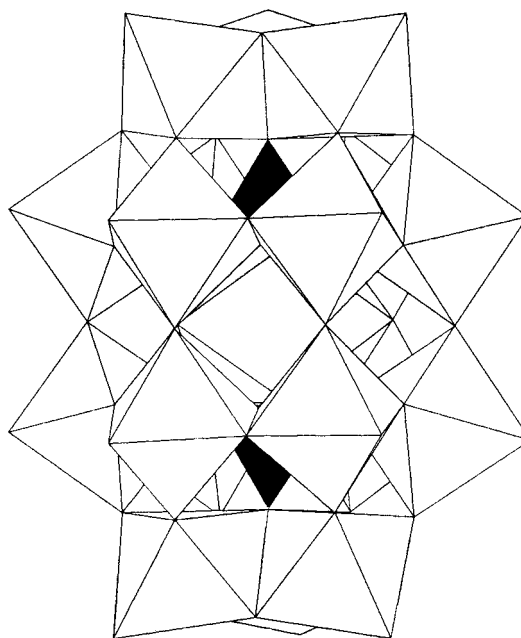
Figure 35. $[As^V_2W_{18}O_{62}]^{6-}$ known as the Dawson structure (X= As^V, P^V). Black tetrahedrons are heteroatom-containing tetrahedrons.

10.15,10.16,11.12,11.17,12.13,12.17,13.14,=
13.18,14.15,14.18,15.16,16.17,16.18,17.18-
hexatriaconta-μ-oxo-μ_9-[tetraoxophosphato(V)-
$O^{1.2.3},O^{4.5},O^{6.7},O^{8.9}$]-$\mu_9$-[tetraoxophosphato(V)-
$O^{10.11},O^{12.13},O^{14.15},O^{16.17.18}$]-
octadecakis(oxotungstate)(6−)

Moreover, it has been observed experimentally that isomers occur resulting from a 60° rotation of the uppermost W_3O_{13} group, or from the upper and the lower W_3O_{13} groups.[50] One thus gets three isomers which may be differentiated by the sequence of locants. As a first step, one may just consider the locants of the heteroatom tetrahedrons.

isomer 1 trivially called αα or α

4.4′,5.5′,6.6′,7.7′,8.8′,9.9′-hexa-μ-oxo-
bis[pentadeca-μ-oxo-μ_9-tetraoxophosphato(V)-
$O^{1.2.3},O^{4.5},O^{6.7},O^{8.9}$-nonakis(oxotungstate)](6−)

isomer 2 trivially called αβ or β

4.4′,5.5′,6.6′,7.7′,8.8′,9.9′-hexa-μ-oxo-[pentadeca-
μ-oxo-μ_9-tetraoxophosphato(V)-
$O^{1.2.3},O^{4.5},O^{6.7},O^{8.9}$-nonakis(oxotungstate)]-
[pentadeca-μ-oxo-μ_9-(tetraoxophosphato(V)-
$O^{1.2.3},O^{4.9},O^{5.6},O^{7.8}$-nonakis(oxotungstate)](6−)

isomer 3 trivially called ββ or γ

4.4′,5.5′,6.6′,7.7′,8.8′,9.9′-hexa-μ-oxo-
bis[pentadeca-μ-oxo-μ_9-tetraoxophosphato(V)-
$O^{1.2.3},O^{4.9},O^{5.6},O^{7.8}$-nonakis(oxotungstate)](6−)

The whole information is given by numbering the whole tungsten skeleton, by putting locants for the bridges, and by showing the bridging locants for the two heteroatom tetrahedrons. The whole series of locants provides a distinction between the three isomers.

isomer 1

1c.2a,1a.3c,1f.4a,1e.9a,2c.3a,2e.5a,2f.6a,3e.7a,=
3f.8a,**4c.5b**,4d.9e,4f.10a,5e.6d,5f.11a,6c.7b,=
6f.12a,7e.8d,7f.13a,8c.9b,8f.14a,9f.15a,10e.11d,=
10b.15c,<u>10f.16c</u>,11c.12b,11f.17b,12e.13d,12f.17c,=
13c.14b,<u>13f.18b</u>,14e.15d,14f.18c,15f.16b,16f.17d,=
16d.18f,17f.18d-hexatriaconta-μ-oxo-μ_9-
[tetraoxophosphato(V)-$O^{1.2.3},O^{4.5},O^{6.7},O^{8.9}$]-$\mu_9$-
[tetraoxophosphato(V)-$O^{10.11},O^{12.13},O^{14.15},O^{16.17.18}$]-
octadecakis(oxotungstate)(6−)

isomer 2

1c.2a,1a.3c,1f.4a,1e.9a,2c.3a,2e.5a,2f.6a,3e.7a,=
3f.8a,**4e.5d**,4b.9c,4f.10a,5c.6b,5f.11a,6e.7d,=
6f.12a,7c.8b,7f.13a,8e.9d,8f.14a,9f.15a,10c.11b,=
10d.15e,<u>10f.16b</u>,11e.12d,11f.16c,12c.13b,12f.17b,=
13e.14d,<u>13f.17c</u>,14c.15b,14f.18b,15f.18c,16f.17d,=
16d.18f,17f.18d-hexatriaconta-μ-oxo-μ_9-
[tetraoxophosphato(V)-$O^{1.2.3},O^{4.5},O^{6.7},O^{8.9}$]-$\mu_9$-
[tetraoxophosphato(V)-$O^{10.11},O^{12.13},O^{14.15},O^{16.17.18}$]-
octadecakis(oxotungstate)(6−)

isomer 3

1c.2a,1a.3c,1f.4a,1e.9a,2c.3a,2e.5a,2f.6a,3e.7a,=
3f.8a,**4e.5d**,4b.9c,4f.10a,5c.6b,5f.11a,6e.7d,=
6f.12a,7c.8b,7f.13a,8e.9d,8f.14a,9f.15a,10c.11b,=
10d.15e,<u>10f.16c</u>,11e.12d,11f.17b,12c.13b,12f.17c,=
13e.14d,13f.18b,14c.15b,14f.18c,15f.16b,16f.17d,=
16d.18f,17f.18d-hexatriaconta-μ-oxo-μ_9-
[tetraoxophosphato(V)-$O^{1.2.3},O^{4.9},O^{5.6},O^{7.8}$]-$\mu_9$-
[tetraoxophosphato(V)-$O^{10.15},O^{11.12},O^{13.14},O^{16.17.18}$]-
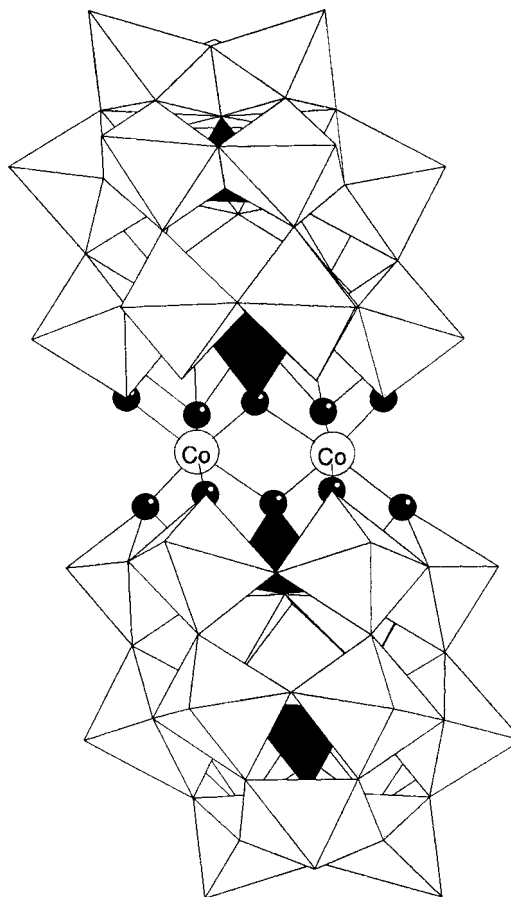octadecakis(oxotungstate)(6−)

Figure 36. $[Co_2(As^V_2W_{15}O_{56})_2]^{20-}$; a Dawson compound has lost a W_3O_6 group. Two $As_2W_{15}O_{56}$ units are ligated to two cobalt atoms by one oxygen atom of As^VO_4 and by four oxygen atoms of the pentadecatungstate unit. The four arsenic-containing tetrahedrons are black. Cobalt atoms are shown as open circles with the Co symbol inside and oxygen atoms octahedrally surrounding cobalt atoms are black.

Bold locants are the first ones to distinguish isomers 2 and 3 from isomer 1, underlined locants are the first ones to distinguish isomers 1 and 3 from isomer 2.

As it happens with the Keggin structure, or its derivatives, the Dawson structure may degradated by taking away some tungsten atoms. For instance, one terminal group W_3O_{13} may be withdrawn and the resulting pentadecatungstate may be used as a ligand onto a dicobalt group, yielding $[Co_2(As^V_2=W_{15}O_{56})_2]^{20-}$ (Figure 36).[51] Actually the two cobalt atoms make a group of two octahedrons sharing an edge. On each side, five oxygen atoms are shared, four bridging tungsten and cobalt atoms, one bridging arsenic(V) and cobalt atoms, as has been already described in section IV.7. The numbering of tungsten atoms starts from the upper terminal skeletal plane containing three tungsten atoms. The name is

bis{1.2,1.3,1.4,1.9,2.3,2.5,2.6,3.7,3.8,4.5,4.9,4.10,=
5.6,5.11,6.7,6.12,7.8,7.13,8.9,8.14,9.15,10.11,=
10.15,11.12,12.13,13.14,14.15-heptacosa-μ-oxo-
[μ_9-tetraoxoarsenato(V)-$O^{1.2.3},O^{4.5},O^{6.7},O^{8.9}$]-
{[μ_6-tetraoxoarsenato(V)-$O^{10.11},O'^{12.13},O''^{14.15}$]-
1,2$\kappa O'''$}-10,11,12,13,14,15-hexaoxo-
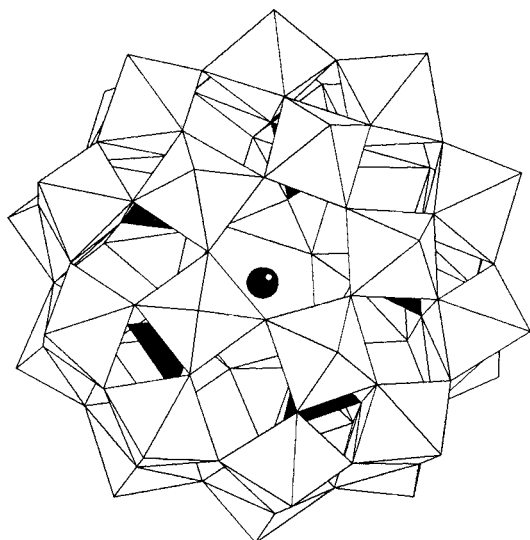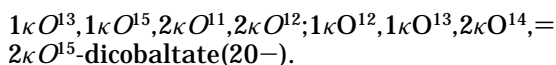pentadecakis(oxotungstato)}-

Figure 37. $[P^V_5W_{30}O_{110}]^{15-}$ is known as the Preyssler compound. The drawing shows the molecular 5-fold axis of symmetry with an ion encapsulated into this doughnut-shaped compound as a black circle; it may be sodium or europium or others. The five phosphorus-containing tetrahedrons are black.
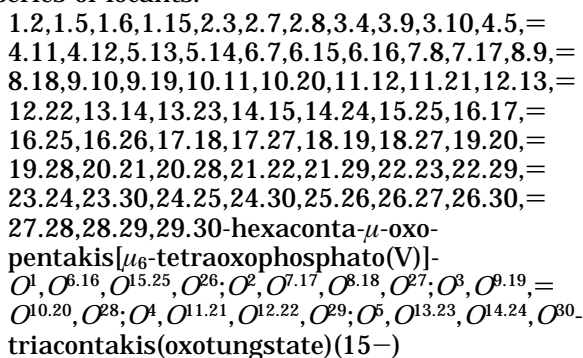
$1\kappa O^{13},1\kappa O^{15},2\kappa O^{11},2\kappa O^{12};1\kappa O^{12},1\kappa O^{13},2\kappa O^{14},=$
$2\kappa O^{15}$-dicobaltate(20−).

$P_2W_{12}O_{48}$ is another fragment which can be obtained by stripping off further the Dawson compound. $[P_8W_{48}O_{184}]^{34-}$ [52] is named as above, using the fact that it may be considered as a ring made of four $P_2W_{12}O_{48}$ units, each unit sharing twice two oxygen atoms with its two neighbors.

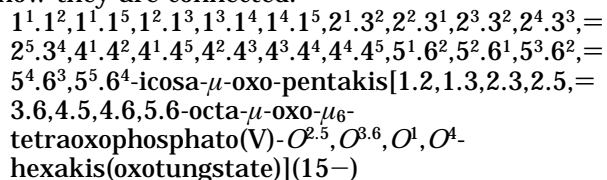## IV.10. Heteropolyanions Containing a Large Number of Tungsten Atoms

$[P_5W_{30}O_{110}]^{15-}$ is the fusion of five PW_6O_{22} groups which are joined together, forming a doughnut-shaped compound which has a 5-fold axis of symmetry (Figure 37).[53] Each PW_6O_{22} group has two such neighboring groups and it shares four oxygen atoms with each of them, so that there are 20 μ-oxo bridges in the whole structure interconnecting five PW_6O_{14} groups. The shortest name is found by counting the oxygen atoms:

hexaconta-μ-oxo-pentakis[μ_6-
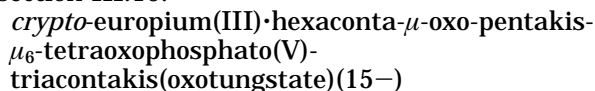tetraoxophosphato(V)-triacontakis=
(oxotungstate)](15−)
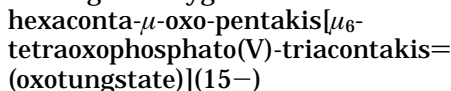
It is impossible to find out how WO_6 octahedrons are assembled. A complete name would require the numbering of all tungsten atoms, leading to a long series of locants.

1.2,1.5,1.6,1.15,2.3,2.7,2.8,3.4,3.9,3.10,4.5,=
4.11,4.12,5.13,5.14,6.7,6.15,6.16,7.8,7.17,8.9,=
8.18,9.10,9.19,10.11,10.20,11.12,11.21,12.13,=
12.22,13.14,13.23,14.15,14.24,15.25,16.17,=
16.25,16.26,17.18,17.27,18.19,18.27,19.20,=
19.28,20.21,20.28,21.22,21.29,22.23,22.29,=
23.24,23.30,24.25,24.30,25.26,26.27,26.30,=
27.28,28.29,29.30-hexaconta-μ-oxo-
pentakis[μ_6-tetraoxophosphato(V)]-
$O^1,O^{6.16},O^{15.25},O^{26},O^2,O^{7.17},O^{8.18},O^{27},O^3,O^{9.19},=$
$O^{10.20},O^{28},O^4,O^{11.21},O^{12.22},O^{29},O^5,O^{13.23},O^{14.24},O^{30}$-
triacontakis(oxotungstate)(15−)

One may also think about showing the 5-fold symmetry using five times a PW_6O_{14} group to which a name is given. Then, a series of μ-oxo bridges show how they are connected.

$1^1.1^2,1^1.1^5,1^2.1^3,1^3.1^4,1^4.1^5,2^1.3^2,2^2.3^1,2^3.3^2,2^4.3^3,=$
$2^5.3^4,4^1.4^2,4^1.4^5,4^2.4^3,4^3.4^4,4^4.4^5,5^1.6^2,5^2.6^1,5^3.6^2,=$
$5^4.6^3,5^5.6^4$-icosa-μ-oxo-pentakis[1.2,1.3,2.3,2.5,=
3.6,4.5,4.6,5.6-octa-μ-oxo-μ_6-
tetraoxophosphato(V)-$O^{2.5},O^{3.6},O^1,O^4$-
hexakis(oxotungstate)](15−)

Such a species encapsulates a variety of cations, e.g., sodium or europium(III), yielding a host-guest compound. The europium compound may be named as follows, according to what has been proposed in section III.10.

crypto-europium(III)·hexaconta-μ-oxo-pentakis-
μ_6-tetraoxophosphato(V)-
triacontakis(oxotungstate)(15−)

V. Concluding Remarks

It has been outlined in the introduction that nomenclature may be considered as a language. The aim of this article has been to show how that the proposed rules work out and how it is possible to use them to build a name. Nevertheless, as it is for any language, it may change over the years. In the case of chemistry, it will result from the progress accomplished by chemists in the synthesis of new compounds displaying unexpected structures which cannot be handled easily by the present set of rules. Indeed the main idea is to connect unambiguously the name of a compound and its structure, and conversely. However as it stands for every language, subsequent development will deal with the form of the language, not with general principles which will remain very much the same. It has been the purpose of this article to show how the various levels of complexity which may be introduced into a name provide chemists several solutions in naming a compound in accord with their needs.

The aim of systematic nomenclature is to provide a name containing a full set of information on composition and structure. Unfortunately polyoxometalates may have complicated structures, sometimes of low symmetry. As a consequence, names showing all these features may become cumbersome and awkward. Central atoms, i.e., metal atoms, have to be numbered and names may contain a long series of numbers. Simpler names may be coined, taking out some details, depending on the level of information to be convened. Such abridged names still remain longer than trivial names. This is why chemists in their everyday discussions prefer to use trivial names because thay are short and convenient. They have been used since the first report of new compounds at a time structures were unknown and impossible to attain; they will be used fairly for a very long time. However they carry no information on the composition nor on the structure, as the name strychnine does for a chemist who is not an organic chemist; everybody has heard about it but to write down the composition or to draw the structure is something else. The use of trivial names remains in the context of polyoxometalates justified; a systematic

name is the clue for a full description of a compound and for retrieval purposes. It was the aim of this article to show how to connect a systematic name with a structure and how to derive such a name, even if the systematic name and the related drawing have to be used side by side when the compound has a complicated framework.

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