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-

† 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 an hyphen would retain the hyphen and those ending with the = would be joined without any further punctuation.

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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 “dub” 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
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 inventive new trivial names exciting our imagination because the known nomenclature system does not provide easy solutions if any. A recent example is given by fullerences. 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. 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.

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

(d) Bridging ligands are indicated by the Greek letter \(\mu\) appearing before the ligand name and separated by a 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 prefix is placed before \(\mu\) and separated by a hyphen, e.g. tri-\(\mu\)-oxo.

The bridging index, i.e., the number of coordination centers connected to one bridging ligand, is indicated by a right subscript \(n\mu\), 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...
in alphabetical order along with other ligands, but a bridging ligand is cited before the nonbridging ligand, e.g. \(\text{oxy-trioxo}\). 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 \(-\text{ate}\) is added after the central atom list; when there is only one atomic species, \(-\text{ate}\) 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 multiplicative prefixes, whatever numbering locants are, enclosed in parentheses with the suffix \(-\text{ate}\) 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.

(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.

(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 skeletal 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, monatomic ligands precede polyatomic ligands with the same ligating atom, e.g., oxygen atoms of OH or $\text{CH}_3\text{COO}$ 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 $\mu_6$.

Lindqvist studied the structure of $\text{Na}_7\text{H}[\text{Nb}_{6}\text{O}_{19}]^{-} = 16\text{H}_2\text{O}$. By concentrating on the name of the polyanion $[\text{Nb}_{6}\text{O}_{19}]^{8-}$, it is sufficient to count oxygen.
atoms of various kinds, i.e., terminal and bridging oxygen atoms, either \( \mu_2 \) and \( \mu_6 \) (Figure 1):

\[
\mu_6\text{-oxo-dodeca-}\mu_\text{-oxo-hexa(oxoniobate)}(8^-)
\]

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

\[
\mu_6\text{-oxo-dodeca-}\mu_\text{-oxo-hexa(oxoniobate)}(8^-)
\]

The use of hyphens and the sequence of \( \mu_6\)-oxo and \( \mu\)-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, \( \mu_6\)-oxo and \( \mu\)-oxo, are designated.

The same principles may be applied without any difficulties to isopolyanions having the same structure, for example, \([\text{Ta}_{6}\text{O}_{19}]^{5-}\), \([\text{Mo}_{6}\text{O}_{19}]^{2-}\), and \([\text{W}_{6}\text{O}_{19}]^{2-}\).

### 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. \([\text{Mo}_{6}\text{O}_{19}]^{2-}\) reduced by one electron is \([\text{Mo}_{6}\text{O}_{19}]^{3-}\):

\[
\mu_6\text{-oxo-dodeca-}\mu_\text{-oxo-hexa(oxomolybdate)}(3^-)
\]

### III.3. Isopolyanions with Five Metal Centers

A family of polyanions containing five metal centers has been found: \([\text{Mo}_{5}\text{O}_{15}(\text{PO}_4)_2]^{6-}\), \([W_{5}\text{O}_{15}]^{6-}\), \([\text{Mo}_{5}\text{O}_{15}(\text{HPO}_4)_2]^{4-}\), and \([\text{Mo}_{5}\text{O}_{15}(\text{SO}_3)_2]^{4-}\). 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:

\[
di-\mu_4\text{-oxo-di-}\mu_3\text{-oxo-octa-}\mu\text{-oxo-decaoxohepta-molybdate}(6^-)
\]

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 \( C_6\text{H}_5=\text{SO}_2^- \) which now is bridging four molybdenum atoms instead of five in \([\text{Mo}_{6}\text{O}_{15}(C_6\text{H}_5\text{SO}_2)_2]^4\cdot\]

\[
penta\text{-oxo-bis-}\mu_4\text{-[dioxophenylsulfato(1-)]-pentakis(dioxomolybdate)(2-)}
\]

### 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 \([\text{Mo}_{7}\text{O}_{24}]^{6-}\) is:

\[
di-\mu_4\text{-oxo-di-}\mu_3\text{-oxo-hexa-}\mu\text{-oxo-octa-}\mu\text{-oxo-decaoxoheptamolybdate}(6^-)
\]

The octamolybdate known as \( \beta\text{-}[\text{Mo}_{8}\text{O}_{26}]^{4-} \) is named as (Figure 3):

\[
di-\mu_4\text{-oxo-tetra-}\mu_3\text{-oxo-hexa-}\mu\text{-oxo-tetradecaoxo-octa-molybdate(4-)}
\]

The \( \alpha\)-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 \([\text{W}_{12}\text{O}_{38}(\text{OH})_2]^{10-}\) (Figure 4) while the other derives from the Keggin structure (vide infra) with the formula \([\text{W}_{12}\text{O}_{38}=(\text{OH})_2]^8\cdot\]

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. \([\text{Mo}_{6}\text{O}_{15}(\text{PO}_4)_2]^{6-}\) 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.](image1)

![Figure 3. The isopolyanion \([\text{Mo}_{8}\text{O}_{26}]^{4-}\) trivially called \(\beta\text{-}[\text{Mo}_{8}\text{O}_{26}]^{4-}\). Oxygen atoms are shown by O inside a circle.](image2)
becoming more complicated but they allow the whole structure to be rebuilt:

di-\(\mu_3\)-hydroxo-tetra-\(\mu_3\)-oxo-octadeca-\(\mu\)-oxo-
octadeca(oxododecatungstate)(10–)
or
di-\(\mu_3\)-hydroxo-di-\(\mu_3\)-oxo-tetracosa-\(\mu\)-oxo-
dodecapakis(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). They are treated as two different metal centers which are cited in the increasing order of oxidation states. The name is

hexadeca-\(\mu_3\)-oxo-dodeca-\(\mu\)-hydroxo-(dodekakis= [oxomolybdenum(V)tetraakis[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.
terminal oxygen atom and each basal oxygen atom is shared between three pyramids, which leads to the following name:
\[
\text{tetracosa-}\mu_3\text{-oxo-octadeca(oxovanadate)}(12-)\text{.}
\]
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:
\[
\text{closo-tetracosa-}\mu_3\text{-oxo-octadeca(oxovanadate}=(IV)\text{)(12-)}
\]
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 subtracts 18 terminal oxygen as shown by the name. Thus 72 oxygen are left which fits with 24 \(\mu_3\)-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.\(^\text{12}\)

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 [\(\text{Nb}_\text{W}_\text{O}_{19}\)]\(^\text{3-}\) is named:
\[
\mu_\text{G}-\text{oxo-dodeca-}\mu_\text{G}-\text{oxo-hexaoxo(niobiumpenta-}
\text{tungsten)ate(3-)}
\]

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.

[\(\text{Nb}_\text{W}_\text{O}_{19}\)]\(^\text{3-}\) 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.

\[
\mu_\text{G}-\text{oxo-dodeca-}\mu_\text{G}-\text{oxo-hexaoxo(tetraniobium-1,2-}
\text{ditungsten)ate(6-)}
\]

\[
\mu_\text{G}-\text{oxo-dodeca-}\mu_\text{G}-\text{oxo-hexaoxo(tetraniobium-1,6-}
\text{ditungsten)ate(6-)}
\]

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 the order; they are enclosed in parentheses and the order, but then 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 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.

### III.7. Nitrosylated and Analogous Compounds

The most simple compound certainly is [\(\text{Mo}_\text{O}_{19}(\text{NO})\)]\(^\text{3-}\) in which one nitrosyl ligand has substituted one terminal oxygen atom (Figure 9).\(^\text{14}\)

\[
\mu_\text{G}(\text{tetraoxovanadato-O,O’,O”,O’”})\text{-tetrakis(}\mu_\text{G}-
\text{tetroxovanadato-O,O’})\text{-tetrakis(}\mu_\text{-oxo-bis(dioxomolybdate)})\text{)(7-)}
\]

Another example is given by the two isomers of [\(\text{V}_\text{W}_\text{O}_{19}\)]\(^\text{4-}\):
\[
\mu_\text{G}-\text{oxo-dodeca-}\mu_\text{G}-\text{oxo-hexaoxo(tetratungsten-5,6-divanadium)ate(4-)}
\]

\[
\mu_\text{G}-\text{oxo-dodeca-}\mu_\text{G}-\text{oxo-hexaoxo(tetratungsten-3,5-divanadium)ate(4-)}
\]

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 [\(\text{NbW}_\text{O}_{19}\)]\(^\text{3-}\):
\[
\mu_\text{G}-\text{oxo-dodeca-}\mu_\text{G}-\text{oxo-hexaoxo(5-niobiumtetratungsten-3-vanadium)ate(4-)}
\]

More complicated species may be named by following the same practice. [\(\text{V}_\text{M}_\text{O}_{19}\)]\(^\text{7-}\) is made of four dinuclear units of molybdenum octahedrons sharing one edge and arranged around a VO\(_4\) tetrahedron (Figure 8).\(^\text{13}\) It is a \(\mu_\text{G}\) tetrahedral ligand because one common vertex of each dinuclear unit is a tetrahedron vertex. Dinuclear units are bound together by another shared edge making an 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 \(\mu_\text{G}\) ligand. Thus the name is written as
\[
\mu_\text{G}(\text{tetraoxovanadato-O,O’,O”,O’”})\text{-tetrakis(}\mu_\text{G}-
\text{tetroxovanadato-O,O’})\text{-tetrakis(}\mu_\text{-oxo-bis(dioxomolybdate)})\text{)(7-)}
\]
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 \( \mu_2 \) oxygen in cis position with respect to the nitrosyl ligand.\(^{15}\) The numbering of vertices is needed to identify the methoxo position:

1d-\( \mu \)-methoxy-1a-nitrosyl-\( \mu_5 \)-oxo-undeeca-\( \mu \)-oxo-pentaoxohexamolybdate(2–)

1d for methoxy 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 the MoNO group with respect to the \( \mu_5 \)-oxo ligand (Figure 10a):

\[
\text{[Rh}_2\text{C}_6\text{H}_8\text{O}_4\text{H}_2\text{O}](\text{Mo}_5\text{MoO}_3\text{O}_7\text{O}_2\text{H}_2\text{O}^+)\]

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\(_2\)C\(_6\)H\(_8\)O\(_4\)H\(_2\)O](Mo\(_5\)MoO\(_3\)O\(_7\)O\(_2\)H\(_2\)O\(_2\))\(^{16}\) is (Figure 10b)\(^{16}\) aqua(pentamethylcyclopentadienyl)(1b,1c,1d,1e-tetra-\( \mu \)-methoxy-1a-nitrosyl-\( \mu_5 \)-oxo-tetra-\( \mu \)-oxo-octaoxopentamolybdate-O\(_2\))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 RhOMoOMo? The use of locants for ligating oxygen atoms makes the name clear and complete:

aqua(pentamethylcyclopentadienyl)(1b,1c,1d,1e-tetra-\( \mu \)-methoxy-1a-nitrosyl-\( \mu_5 \)-oxo-tetra-\( \mu \)-oxo-octaoxopentamolybdate-O\(_2\))rhodium(1–)

The same type of compound may be prepared with silver. Two silver atoms get a square-planar environment of four oxygen atoms without any silver-silver bond, which implies two Mo\(_2\) units:\(^{17}\) bis(1b,1c,1d,1e-tetra-\( \mu \)-methoxy-1a-nitrosyl-\( \mu_5 \)-oxo-tetra-\( \mu \)-oxo-octaoxopentamolybdate)-O\(_2\)O\(_2\)O\(_2\)O\(_2\)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\(_5\)O\(_3\)O\(_7\)O\(_2\)H\(_2\)O\(_2\))\(^{18}\). The two nickel ones share an edge with two \( \mu \)-oxhydroxo 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) polioxometalate ligand as in the preceding rhodium complex (Figure 10c).\(^{17}\) Thus the name is

di-\( \mu_3 \)-hydroxo-tetra-\( \mu \)-methanol-dimethanol =

\[
\text{dinitrosylbis(1b,1c,1d,1e-tetra-\( \mu \)-methoxy-1a-nitrosyl-\( \mu_5 \)-oxo-tetra-\( \mu \)-oxo-octaoxopentamolybdate)-O\(_2\)}\]

This does not say which ligands are bound to nickel and which ligands are bound to molybdenum in the four metal Mo\(_5\)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 \( \kappa \) 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\(_5\)Ni\(_2\) core and the numbering of the Mo\(_5\)(NO) ligand.

\[
\text{di-\( \mu_3 \)-hydroxo-tetra-\( \mu \)-methanol-dimethanol =}
\]

This type of substitution occurs with an imidato ligand. Phenylimidato provides a structure (Figure 11). It may be described

\[
\text{[Mo}_6\text{O}_{18}(\text{NO})]^{3–}
\]

Figure 9. [Mo\(_5\)O\(_{18}\)(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.
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$_2$O)$_8$ which contains six types of molybdenum surroundings (Figure 12). One may just name the various types of ligands with their bridging feature:

di-$\mu$-aqua-hexaaquadinitrosyldi-$\mu$-oxo-deca-$\mu$-oxo-tetradeca-$\mu$-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($\mu$-hexaaxomolybdate-O,O':O'',O''')-bis(di-$\mu$-aqua-hexaaquadinitrosyldi-$\mu$$_4$-oxo-deca-$\mu$$_3$-oxo-

tetradeca-$\mu$-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($\mu$-hexaaxomolybdate)-O$_{1,1}$,O$_{2,2}$,O$_{3,3}$,O$_{6,6}$-

bis(10.13,11.12-di-$\mu$-aqua-1,2,3,4,5,6-hexaaqua-
7,8-dinitrosyl-7.9.14.15,8.9.16.17-di-$\mu$-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-$\mu$$_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-$\mu$-oxo-
In such a name, 10.13,11.12-di-\textit{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\textsubscript{5}V\textsubscript{6}O\textsubscript{18}(OH)\textsubscript{3}(NO)\textsubscript{6}(H\textsubscript{2}O)\textsubscript{18}]	extsuperscript{24-}\textsuperscript{24-} is a three Mo\textsubscript{17} building blocks named as above and assembled in a ring; this is shown by cyclo-\textit{tris} in the name. They are connected by three complex bridges. Each bridge is made of one Mo\textsubscript{3}O\textsubscript{6}=(\mu-OH)(\mu-H\textsubscript{2}O)\textsubscript{2} dinuclear unit and two V\textsubscript{O}\textsubscript{3}(H\textsubscript{2}O) octahedrons which will be treated as ligands; each bridging group is bound to four molybdenum atoms, two of the right Mo\textsubscript{17} unit, and two of the left Mo\textsubscript{17} unit; this is shown by \textit{\mu}_4-(...-O,O',O'',O''') in the name: cyclo-tris\{bis-\textit{\mu}_4-(aqapentaaoxovanadato-0,O',O'',O''')(\mu-\textit{\mu}_4-aqua-\textit{\mu}-hydroxo-bis(trioxomolybdate)-O,O':O'',O''')(\text{diaqua}=dinitroso\textit{\mu}_4-oxo-deca-\textit{\mu}_3-oxo-tetradeca-\textit{\mu}-oxo-icosaoxoheptadecamolybdate)}\textsuperscript{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.

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),\textsuperscript{21} iodine(VII). The polyanion has a ternary axis and the formula is [MM\textsubscript{4}O\textsubscript{24}]n-. An isomer [Mo\textsubscript{7}O\textsubscript{24}]\textsuperscript{6-} occurs which has C\textsubscript{2v} symmetry. Citing all the oxygen atoms leads straightforwardly to the structure of [TeMo\textsubscript{6}O\textsubscript{24}]\textsuperscript{6-}. A strict application of coordination compounds nomenclature rules requires an alphabetical sequence of symbols for cations, i.e. Mo-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 [XM\textsubscript{6}O\textsubscript{24}]\textsuperscript{6-} is preferred:

hexa-\mu\textsubscript{3}oxo-hexa-\mu-oxo-dodecaoxo(hexa=molybdenum-7-tellurium)ate(6-) or

hexa-\mu\textsubscript{3}oxo-hexa-\mu-oxo-[hexakis(dioxo=molybdenum)-7-tellurium]ate(6-)
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 $[\text{Mo}_7\text{O}_{24}]^{6-}$ is (see section III.4)

$$\text{di}_{\mu_2-\text{oxo-di}_{\mu_3-\text{oxo-octa-\mu}_2-\text{oxo-dodecaoxohepta-}}\text{molybdate}(6^-)$$

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:

$$\text{hexa}_{\mu_3}-\text{hydroxo-hexa}_{\mu_2-}\text{oxo-[7-chromiumhexa-}}\text{kis(dioxomolybdenum)]ate(6^-)$$

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:

$$\text{hexa}_{\mu_3}-\text{hydroxo-hexa}_{\mu_2-}\text{oxo-[7-chromium(III)hexakis(dioxomolybdenum)]ate(6^-)$$

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

$$\text{hexahydrogenhexa}_{\mu_3}-\text{oxo-hexa}_{\mu_2-}\text{oxo-[7-chromium(III)hexakis(dioxomolybdenum)]ate(6^-)$$

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) $\text{AsO}_4^{3-}$, or a tetraoxomolybdate(V) $\text{MoO}_4^{2-}$, or a methyltrioxoarsenate(V) $\text{C}_5\text{H}_5\text{AsO}_3^{3-}$. Names are bis-$\mu_2$-(tetraoxoarsenate-$O'_2$,O’,-)-hexa-$\mu_2$-oxo-hexamolybdate(6–)

bis-$\mu_3$-(methyltrioxoarsenate-$O'_3$,O’,-)-hexa-$\mu_2$-oxo-hexamolybdate(6–)

bis-$\mu_2$-(tetraoxomolybdate-$O'_4$,O’,-)-hexa-$\mu_2$-oxo-hexamolybdate(6–)

The two tetrahedrally surrounded molybdenum atoms could be as well included into the metal framework which would then count eight molybdenum atoms. Treating $\text{MoO}_4$ as a ligand produces a simpler name, makes clear the structural relationship, and thus is preferred (Figure 14).

There is an Anderson structure based on a CoW$_6$ skeleton with two cyclotriarsenite, one on each side of the crown, $[\text{CoW}_6\text{As}_6\text{O}_{30}]^{4-}$ (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 $\mu_7$-

$\text{hexa}_{\mu_6}$-oxo-bis-$\mu_7$-[tri-$\mu_3$-oxotris(oxoarsenate)(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 $[\text{MnMo}_6\text{O}_{18}\{\text{CH}_3\text{C}=(\text{CH}_2\text{O})_3\}_2]^{22}$ which contains a capping triol (Figure 16a).24

bis-$\mu_7$-[neopentane-1,2,3-triolato-O,O’,O’’]-hexa-$\mu_2$-oxo-[7-manganese(II)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 $[\text{ZnMo}_6\text{O}_{18}\{\text{CH}_3\text{C}(\text{CH}_2\text{O})_3\}_2]^{4-}$ for which the CH$_3$C axis of the triol is not any longer...
the ternary axis of the Anderson basic structure but it is parallel to it (Figure 16b). 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:

\[
\text{bis} \cdot \mu_5\text{(neopentane-1,2,3-triolato-O,O',O'')-di-\mu_3-oxo-tetra-\mu-oxo-hexakis(dioxomolybdenum)-7-zincate(4–)}
\]

Another compound \([\text{Mo}_8\text{O}_{24}\{\text{CH}_3\text{C(CH}_2\text{O)}_3\}^2]^{6–}\) containing the same triol now capping three edge-sharing molybdenum octahedrons is known (Figure 16c). Two triol–MoO6 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:

\[
\text{bis} \cdot \mu_5\text{(neopentane-1,2,3-triolato-O,O',O'')-di-\mu_3-oxo-octa-\mu-oxo-tetradecaaoxooxocatamylbdate(6–)}
\]

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

\[
\text{bis} \cdot \mu_5\text{-hexaoxomolybdatato-O,O',O'',O'''}\text{-bis} \cdot \mu_3\text{-oxo-pentaaoxotrimolybdate(6–)}
\]

This name has the advantage of pointing out that there are two equivalent triol–MoO6 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 \([\text{W}_6\text{O}_{18}\text{S}]^{2–}\)

\[
\mu_6\text{-oxo-dodeca-\mu-oxo-pentaoxothiohexa-tungstate(2–)}
\]

contains one terminal sulfur atom, \(\mu_6\text{-oxo-undeca-\mu-oxo-\mu-thio-hexakis(oxo=tungstate(2–)}\)

contains one bridging sulfur atom. The name \(\mu_6\text{-oxo-dodeca-\mu-oxo-pentaaoxo-1a-thio(6-niobiumpentatungsten)ate(3–)}\)

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 \(\mu_6\) oxygen atom. Metal numbering has priority over ligand numbering.

Another example is given by \([\text{W}_3\text{OS}_8]^{2–}\) (Figure 17a). 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:

\[
\text{oxobis(tetrathiotungstato-S,S')tungstate(2–)}
\]

The same type of compound \([\text{W}_4\text{S}_{12}]^{2–}\) occurs with two square pyramids sharing one edge, each of them being bound to a tetrahedron WS4 (Figure 17b):

\[
\text{bis(tetrathiotungstato-S,S')di-\mu-thio-bis(thiotungstate(2–))}
\]
Some mixed compound containing copper and tungsten may be prepared. Their names are simple to build up. For instance $\text{[WCu}_3\text{Cl}_3\text{S}_4\text{]}^2^-$ is made of three WCuS$_2$ squares sharing WS edges so that the central tungsten atom is tetrahedally surrounded by sulfur. Symbols of the elements are written inside open circles.

A dicubane structure $\text{[Cu}_4\text{W}_2\text{Cl}_3\text{S}_8\text{]}^2^-$ is not more difficult to name.

---

**Figure 17.** (a) $\text{[W}_3\text{OS}_8\text{]}^2^-$ 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) $\text{[W}_4\text{S}_{12}\text{]}^2^-$ is made of two square pyramids sharing one edge and two tetrahedrons treated as ligands to square-pyramidal tungsten atom. (c) $\text{[Cu}_3\text{WCl}_3\text{S}_4\text{]}^2^-$ is made of three CuWS$_2$ squares sharing WS edges so that the central tungsten atom is tetrahedally surrounded by sulfur. Symbols of the elements are written inside open circles.

---

**Figure 18.** The cyclical hexamer $\text{[Mo}_{12}\text{O}_{24}\text{S}_{12}(\text{H}_2\text{O})_6\text{]}$. Black circles are molybdenum atoms. Symbols of oxygen and sulfur atoms are inside open circles. Open circles without symbols are water molecules.

\[
\text{di-}\mu^3\text{-thio-tetra-}\mu^3\text{-thio-[tetrakis(chlorocopper)bis(thiotungsten)]ate}(2^-)
\]

As long as the structure is symmetrical and does not raise any special assignment, the name is found in a straightforward manner. For example, $\text{[Mo}_2\text{O}_2\text{S}_6\text{(H}_2\text{O})_6\text{]}$ is a cyclical hexamer (Figure 18) based upon the $\text{O=Mo(\mu-O)}_2(\mu^4\text{H}_2\text{O})\text{Mo=O fragment}$ bridged on each side by two sulfur atoms:

\[
\text{crypto-hexakis(di-}\mu^3\text{-thio-[\mu-aqua-di-\mu-oxo-bis(oxomolybdate(VI))]}^3\text{III.10. Host-Guest Compounds}
\]

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$_3$CN with $\text{[V}_{12}\text{O}_{32}\text{]}^4^-$ is named:

\[
\text{crypto-acetonitrile-octaoxo-dodeca-\mu-oxo-dodecakis(oxovanadate)(4^-)}
\]

Similarly $\text{[H}_4\text{V}_{12}\text{O}_{32}\text{]}^3^-$ enclosing either a chloride or a water molecule will be named:

\[
\text{crypto-aqua-tetrahydrogentetracosa-\mu_3-oxo-octadecakis(oxovanadate)(6^-)}
\]

\[
\text{crypto-chloride-tetrahydrogentetracosa-\mu_3-oxo-octadecakis(oxovanadate)(8^-)}
\]
Taking a different type of compounds, \([\text{Na}_2\text{Fe}_{18}\text{S}_{30}]^{8-}\), the two structurally different host–guest sodium containing polythioferrates will be named 30

crypto-disodium-dodeca-\(\mu_3\)-thio-octadeca-\(\mu\)-thio-octadecaferrate\(\text{(10-)}\)

crypto-disodium-di-\(\mu_4\)-thio-octa-\(\mu_3\)-thio-icosa-\(\mu\)-thio-octadecaferrate\(\text{(10-)}\)

**IV. Heteropolyanions**

Heteropolyanions are those polyanions and their derivatives made of an assembly of fused MO₆ 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 \([\text{PMo}_{12}\text{O}_{40}]^{3-}\). The structure of a similar compound, i.e., \([\text{PW}_{12}\text{O}_{40}]^{3-}\), 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 \([\text{XM}_{12}\text{O}_{40}]^{n-}\) was born. X may be B, Si, Ge, P, As, and some other atoms. M is either molybdenum or tungsten. Several names have been used, besides the trivial name “Keggin compound”. For instance, \([\text{SiW}_{12}\text{O}_{40}]^{4-}\) 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 \(\text{M}_3\text{O}_{13}\) groups are arranged around the heteroatom which is tetrahedrally surrounded. A \(\text{M}_3\text{O}_{13}\) 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 \(\mu_{12}\) bridging ligand. Two \(\text{M}_3\text{O}_{13}\) share two corners. Thus a name based on the formula is

hexatracontaoxo(tetraoxosilicato)dodeca-

tungstate\(\text{(4-)}\)

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

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

tetraoxosilicato-\(\mu\)-oxo-dodecaoxo-\(\mu_{12}\)-tetraoxosilicate-

dodecatungstate\(\text{(4-)}\)

or

tetraoxosilicato-\(\mu\)-oxo-\(\mu_{12}\)-tetraoxosilicate-dodecakis=

(oxotungstate)\(\text{(4-)}\)

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

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. = 5.6.5.10.6.7.11.7.8.7.11.8.9.8.12.9.12.10.11. = 10.12.11.12-tetraoxosilicato-\(\mu\)-oxo-\(\mu_{12}\)-

tetraoxosilicato-\(\text{O}^{1.4.9}\) \(\text{O}^{2.5.6}\) \(\text{O}^{3.7.8}\) \(\text{O}^{10.11.12}\)-

dodecakis(oxotungstate)\(\text{(4-)}\)

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-\(\mu\)-oxo. The most complete and most precise name, but of course also longer and cumbersome, is

\[
1c.2b,1b.3c,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-tetraoxosilicato-\(\mu\)-oxo-\(\mu_{12}\)-

tetraoxosilicato-\(\text{O}^{1.4.9}\) \(\text{O}^{2.5.6}\) \(\text{O}^{3.7.8}\) \(\text{O}^{10.11.12}\)-

dodecakis(oxotungstate)\(\text{(4-)}\)

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.
Such a method has another great advantage. The structure described by Keggin is often trivially called the \( \alpha-[\text{SiW}_{12}\text{O}_{40}]^{4-} \). It has been found that a \( \text{M}_3\text{O}_{13} \) group may be turned by 60° around its C\(_3\) axis. This isomer is trivially called \( \beta-[\text{SiW}_{12}\text{O}_{40}]^{4-} \) (Figure 20). 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 \([\text{SiW}_{12}\text{O}_{40}]^{4-}\) for the sake of clarity.

**isomer 1**, Keggin structure, \( \text{T}_d \) 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-\( \mu\)-oxo-\( \mu\)-dodecakis(oxotungstate)(4-)

dodecakis(oxotungstate)(4-)

**isomer 2**, \( \text{C}_{3v} \) 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,\( \textbf{5.11} \),6.7,6.11,7.8,7.12,8.9,8.12,9.10,10.11,= 10.12,11.12-tetracosa-\( \mu\)-oxo-\( \mu\)-dodecakis(oxotungstate)(4-)

dodecakis(oxotungstate)(4-)

**isomer 3**, two groups turned by 60°
1.2,1.3,1.4,1.5,2.3,2.6,3.6,3.7,3.9,4.5,4.7,4.10,= 5.8,5.11,6.8,6.12,7.9,7.10,8.11,8.12,9.10,12,= 10.11,12,11,12-tetracosa-\( \mu\)-oxo-\( \mu\)-dodecakis(oxotungstate)(4-)

dodecakis(oxotungstate)(4-)

**isomer 4**, three groups turned by 60°
1.2,1.3,1.4,\( \textbf{1.6} \),2.3,2.4,2.5,3.5,3.6,4.7,4.8,5.9,= 5.10,6.11,6.12,7.8,7.12,7.12,8.9,9.10,10.11,= 10.11,11,12-tetracosa-\( \mu\)-oxo-\( \mu\)-dodecakis(oxotungstate)(4-)

dodecakis(oxotungstate)(4-)

**isomer 5**, four groups turned by 60°
1.2,1.3,1.4,\( \textbf{1.6} \),2.3,2.5,2.5,3.6,3.6,4.7,4.12,5.8,= 5.9,6.10,6.11,7.8,7.8,7.12,8.9,9.10,10.11,

![Figure 20](image1.png)

**Figure 20.** The Keggin structure opened with locant assignment. Circles mean that the two related vertices are fused.

![Figure 21](image2.png)

**Figure 21.** Five isomers of \( \text{XM}_{12}\text{O}_{40} \), only the 12 tungsten metal atom frameworks are shown: 1 is the Keggin structure; 2 has one \( \text{M}_3\text{O}_{13} \) 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-\( \mu\)-oxo-\( \mu\)-dodecakis(oxotungstate)(6-)

dodecakis(oxotungstate)(6-)

In the preceding names, bold underlined locants point out the first locant difference with respect to the Keggin compound of \( \text{T}_d \) symmetry.

At this point, it should be remembered that the central position may not be occupied by an heteroatom, but by two hydrogen atoms which then make two \( \mu_3\)-hydroxo and two \( \mu_3\)-oxo ligands. The \( \alpha \)-isomer of \( \text{T}_d \) symmetry is trivially known as the metatungstate:

1.4.9.2.5.6-di-\( \mu_3\)-hydroxo-\( \mu_3\)-dodecakis(oxotungstate)(6-)

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.
It has been shown that the six electrons are localized are WIV.37 It has to be noted that the priority for numbering does not change with respect to the 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-[12-tetraoxosilicato-\(\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\·
hexadecaoxo[oxoarsenato(3−)]bis=[tetraoxoarsenato(5−)][octakis(oxomolybdenum)]=tetraoxoarsenato(5−)

Tetraoxoarsenato(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 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}]^{5−}, one gets the following names:

1.2.1.3.4.2.7.2.8.3.4.3.8.3.9.4.5.4.10.5.6.= 5.10.6.7.6.11.7.8.7.11.8.9.9.10.9.11.10.11-
icosa-μ-oxo-M_{11}-(tetraoxosilicato-
10.12.11-tetraoxosilicato-10.11.12)-dodecaoxoundecatungstate(8−)

To distinguish between isomers, a more detailed name is needed. It implies numbering of tungsten atoms which has first the fewest number of central atoms and second the less condensed situation. 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:

icos-μ-oxo-M_{11}-(tetraoxosilicato-
10.11.12)-dodecaoxoundecatungstate(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:

1.2.1.3.4.5.2.6.2.7.3.4.3.8.3.9.4.5.4.10.5.6.5.10.= 6.7.6.11.7.8.7.11.8.9.9.10.9.11.10.11-
icosa-μ-

oxo-M_{11}(tetraoxosilicato-O^{3−},O^{6.7}.O^{3.8},O^{9.10.11})-

dodecaoxoundecatungstate(8−)

In the last case, which actually is observed experimentally, one can fill the vacancy with one molybdenum atom. 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:

1.2.1.3.4.5.2.6.2.7.3.4.3.8.3.9.4.5.4.10.5.6.5.10.= 6.7.6.11.7.8.7.11.8.9.9.10.9.11.10.11-
icosa-μ-

oxo-M_{11}(tetraoxosilicato-O^{3−},O^{6.7}.O^{3.8},O^{9.10.11})-

dodecaoxoundecatungstate(8−)

IV.4. Compounds with One Vacant Metal Site

One metal atom may be missing yielding an 11 metal atom polyoxotungstate, [SiW_{11}O_{39}]^{5−}. 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_{12}O_{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 opposite to the turned M_{12}O_{13} group.

The rules stated in section II.3 require that the numbering starts from the preferred skeletal plane which has first the fewest number of central atoms and second the less condensed situation. 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:

icos-μ-oxo-M_{11}-(tetraoxosilicato-
10.11.12)-dodecaoxoundecatungstate(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:

1.2.1.3.4.5.2.6.2.7.3.4.3.8.3.9.4.5.4.10.5.6.5.10.= 6.7.6.11.7.8.7.11.8.9.9.10.9.11.10.11-
icosa-μ-

oxo-M_{11}(tetraoxosilicato-O^{3−},O^{6.7}.O^{3.8},O^{9.10.11})-

dodecaoxoundecatungstate(8−)

In the last case, which actually is observed experimentally, one can fill the vacancy with one molybdenum atom. 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:

1.2.1.3.4.5.2.6.2.7.3.4.3.8.3.9.4.5.4.10.5.6.5.10.= 6.7.6.11.7.8.7.11.8.9.9.10.9.11.10.11-
icosa-μ-

oxo-M_{11}(tetraoxosilicato-O^{3−},O^{6.7}.O^{3.8},O^{9.10.11})-

dodecaoxoundecatungstate(8−)
tungstates are known. 21

bound to the second rhodium atom. O first rhodium atoms, and that the oxygen atoms bound to a dirhodium core. 38 The name is straight-forwardly 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-[1.2.1,3.4.2,7.8,3.4.8,3.9.4.5.10.5.6, = 5.10.6.7,6.11.7.8,7.11.18.9.9.10.9.11.10.11-icosahedron of one undecatungstate, so that the hexatungsten-octahedron of the bridge is connected to two tungsten atoms of one undecatungstate, another oxygen 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 M3O13 group, or from the lower skeletal plane, i.e., from three different M3O13 groups (Figure 24). The first case occurs with an heteroatom such as P, or As, because their four surrounding oxygen atoms are still connected to metal atoms. The second case occurs with an heteroatom such as AsIII or SbIII because the lone pair needs some free space. The first case is trivially called type A. An example is [PMo9O28(OH)6]3−, the name of which is (compound III) (Figure 25).

Figure 23. Drawing of [B3W39O132]21-. The three black tetrahedrons contain boron atoms.

The lacunar compound [PW11O39]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-[1.2.1,3.4.2,7.8,3.4.8,3.9.4.5.10.5.6, = 5.10.6.7,6.11.7.8,7.11.18.9.9.10.9.11.10.11-icosahedron of one undecatungstate, so that the hexatungsten-octahedron of the bridge is connected to two tungsten atoms of one undecatungstate, another oxygen 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

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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 M3O13 group, or from the lower skeletal plane, i.e., from three different M3O13 groups (Figure 24). The first case occurs with an heteroatom such as P, or As, because their four surrounding oxygen atoms are still connected to metal atoms. The second case occurs with an heteroatom such as AsIII or SbIII because the lone pair needs some free space. The first case is trivially called type A. An example is [PMo9O28(OH)6]3−, the name of which is (compound III) (Figure 25).
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. \([\text{AsIIIW}_{9}\text{O}_{33}]^{9-}\) is named (compound I):41

One may see that \(\mu\)-oxo bridges have the same numerical locants but they differ when literal locants are added; the numbering of the \(\mu_9\) bridge is also different.

As it happens for the Keggin structure, one may turn one \(\text{M}_{3}\text{O}_{13}\) group by 60°, which yields isomers trivially designated as A̅ and B̅ while the preceding ones are Aα and Bα. They are systematically named as

\[\text{SiW}_{9}\text{O}_{34}^{10-}\text{ with a group turned by 60° (compound IV)}\]

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-\(\mu\)-oxo-pentadecaoxo-\(\mu_9\)-[trioxoaarsenato(III)-O\(\{1\},2,3\},O\(\{4\},6,7\},O\(\{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 \(\mu\)-C\(\text{H}_{3}\)\(\text{PO}_{4}\)\(\{2\}\), yielding \([\text{PVW}_{8}\text{O}_{26}(\text{C\(\text{H}_{3}\)\(\text{PO}_{4}\})_{2}]^{6-}\) (Figure 26). \(\text{The nonatungstate} \text{PW}_{9}\text{O}_{34}\) is derived from the Keggin structure (compound I, type Aα). It is named

\[\text{bis[\(\mu\)-ethyl phosphonato-}\(\mu\)\text{-O,O′]pentadeca-\(\mu\)-oxo-dioxo-\(\mu_9\)-[tetraoxophosphato(V)]-nonakis(oxomolybdate)(6–)\]

or to be more accurately

\[\text{bis(}\mu\)-ethyl phosphonato\text{-O,O′\text{[pentadeca-\(\mu\)-oxo-}
\[\mu_9\]-[tetraoxophosphato(V)]-O\(\{1\},2,3\},O\(\{4\},6,7\},O\(\{8\},9\}]-
\text{nonatungstate(6–)\]

4,5-Dioxo is so numbered because O has priority over C\(\text{H}_{3}\)\(\text{PO}_{4}\)\(\{2\}\). \(\text{tBuSiO}_{2}(\text{OH})_{2}\) or \((\text{C\(\text{H}_{5}\})_{2}\text{SiO}_{2}\text{O})\) behave the same way and names may be derived similarly.42

The same type of compound may be prepared with a tripod-shaped ligand \(\text{C}\(\text{H}_{2}\)\text{Si}[\text{OSi(C\(\text{H}_{5}\)\text{O})_{2}]_{3}\text{SiC\(\text{H}_{2}\)\text{SiO}}_{2}\text{O})_{3}\)6. Each diolate is bound to two tungsten atoms as above and the nonatungstate is the same (Figure 27), the formula is \([\text{PVW}_{8}\text{O}_{28}\{\text{C\(\text{H}_{5}\)\text{Si}[\text{OSi(C\(\text{H}_{5}\)\text{O})_{2}]_{3}\text{SiC\(\text{H}_{2}\)\text{SiO}}_{2}\text{O})_{3}\}^{3-}\]

\[\mu_6\text{-ethyl silanetri[s{oxy(ethyl)silanediolato}-}4\text{-O},5\text{-O},2\text{-O},7\text{-O},3\text{-O},9\text{-O}^{\{1\},2,3,4,9\},O\{5\},6,7,8\}]-
\text{nonatungstate(6–)\]

One may see that \(\mu\)-oxo bridges have the same numerical locants but they differ when literal locants are added; the numbering of the \(\mu_9\) bridge is also different.

As it happens for the Keggin structure, one may turn one \(\text{M}_{3}\text{O}_{13}\) 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

\[\text{ASIIIW}_{9}\text{O}_{33}^{9-}\text{ with a group turned by 60° (compound I)}\]
2.3,2.5,2.6,3.7,3.8,4.5,4.9,5.6,6.7,7.8,8.9-pentadeca-İ-oxo-İ9-[tetraoxophosphato(V)-O1.2.3, O4.5, O6.7, O8.9]-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 M3O13 group (compound 2, type B). 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:

μ6-ethylgermanetris[oxy(tertiobutyl)silanediolato]-4:kO1,5:kO1,6:kO2,7:kO2,8:kO3,9:kO3-

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 C2H3Ge[OSi(CH2)6SiO2]-group.

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

[H2AsW18O60]7- is made of two nine tungsten atom units, one containing an arsenic(III) atom, i.e., AsW9O33, the other containing two hydrogen atoms, i.e., H2W9O33. They both derive from a Keggin structure of which a W3O13 group has been taken away (compound 2, type B). Those two units share six oxygen atoms. The same type of compound occurs with antimony that is [H2SbW18O60]7-. 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).
Simple names such as dihydrogen(trioxoarsenato)heptapentacontaoctadecatungstate(7-)
and dihydrogen(trioxostibato)heptapentacontaoctadecatungstate(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-\(\mu_3\)-hydroxo-3.7.8-\(\mu_3\)-oxo-
1.2.13,1.4.19,2.3.2.5,2.6.3.7.8.4.5.4.9.4.10,=
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-

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 [\(\text{H}_2\text{As}^{III}_2\text{W}_{21}\text{O}_{69}(\text{H}_2\text{O})\)]\(\text{μ}_6\) is made of two As\(^{III}\)-containing nonatungstates (isomer 1) joined by one octahedron WO\(_6\) and two square pyramids WO\(_5\). Black circles are oxygen atoms of the connecting WO\(_5\) octahedron and both WO\(_5\) square pyramids. The water molecule is at the right of the figure.

hexatriaconta-\(\mu\)-oxo-\(\mu_2\)-[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-\(\mu_3\)-hydroxo-3.7.8-\(\mu_3\)-oxo-
1.2.13,1.4.19,2.3.2.5,2.6.3.7.8.4.5.4.9.4.10,=
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-\(\mu\)-oxo-\(\mu_2\)-[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.
A more elaborate name describing the accurate location of all the oxygen atoms in order to be able to reconstruct the structure is

$$\mu_4\text{-aquapentaoxotungstato-}4k_5O_5O'_{4}\text{'s} \cdot \text{bis}[\mu_4\text{-pentaoxotungstato-}4k_5O_5O'_{4}\text{'s}] - \text{bis}1.2.1.3.1.4.1.9.2.3.2.5.2.6.3.7. = 3.8.4.5.4.9.5.6.7.7.8.8.9\text{-pentadeca-}\mu_4\text{-oxo-}\mu_5\text{-oxo-}2\text{,}3\text{,}4.5.6.7.8.9\text{-oxotungstato-}O_3O_5O_6O_7O_9.$$  

The numbering of each W9 unit is the same because they are structurally identical and consequently numbered independently; hence, bis is put in front of the W9 unit name. However to distinguish the ligated sites of the first and of the second unit, 4 and 4′ have been used, 4 for W9 unit number one and 4′ for unit number two.

The nonatungstate unit SbIIIW9O33 is found into the [H2SbIII2W22O76]12− polytungstate (Figure 32). It may described as two SbIIIW9O33 groups in which one W9O33 group has turned by 60°, i.e., it corresponds to compound 4, type Bβ. The W9 skeleton has lost its C3 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 SbIIIW9O33 units are bound by four octahedrons, two WO6 and two WO5(OH) octahedrons. A locant assignment of the W9 units is necessary to make clear the way those octahedrons bridge the units.

The structure [AsVW12O40]3− has been used, 4 for W9 unit number one and 4′ for unit number two.

Another more difficult case (Figure 33) is a Keggin structure [AsVW12O40]3− which has lost a group W2O13, yielding the fragment [AsVW9O34]8−, similar to compound 2, type Bα, with however an arsenic(V) bearing a pending oxygen atom instead of an arsenic(V) atom. Two such groups are ligated to a group of four cobalt-centered octahedrons sharing edges and making a Co4O14(H2O)2 fragment. Seven oxygen atoms are shared between this group and AsVW9O34.
six being ligated to tungsten and one to arsenic. The formula is $[\text{Co}_4(\text{As}^\text{III}_2\text{W}_9\text{O}_{34})_2(\text{H}_2\text{O})_2]^{10-}$. A name might be diaquabis($\mu_4$-tetraoxoarsenato(V)-pentadeca-$\mu$-oxo-pentadecaonatungstato(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 $\kappa$ convention, hence to number on one hand the $W_9$ unit and on the other hand the $\text{Co}_4$ unit. Thus two sets of locants run 1 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 of the metal framework becomes necessary. The name, simple in principle, but more difficult to read because of the long series of locants, section

Figure 34. $[\text{As}^{\text{III}}_3\text{W}_9\text{O}_{33}(\text{OH})]^{16-}$. This is a fragment of $\text{As}^{\text{III}}_3\text{W}_9\text{O}_{33}$ in which a $W_9\text{O}_{33}$ group turned (isomer 2) from which one tungsten atom was withdrawn. In addition a $\text{As}^{\text{III}}_2\text{O}_2(\text{OH})$ 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. $[\text{As}^{\text{III}}_2\text{W}_9\text{O}_{33}]^{16-}$ known as the Dawson structure (X= As$^{\text{III}}$, P$^{\text{V}}$). Black tetrahedrons are heteroatom-containing tetrahedrons.
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. 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 $\alpha\alpha$ or $\alpha$

$4.4',5.5',6.6',7.7',8.8',9.9'$-hexa-$\mu$-oxo-[pentadeca-$\mu$-oxo-$\mu_3$]-tetraoxophosphato(V)-$O_1^{1.2.3},O_4^{4.5},O_6^{6.7},O_9^{9.10}$-nonakis(oxotungstate)(6–)

**Isomer 2** trivially called $\beta\beta$ or $\beta$

$4.4',5.5',6.6',7.7',8.8',9.9'$-hexa-$\mu$-oxo-[pentadeca-$\mu$-oxo-$\mu_3$]-tetraoxophosphato(V)-$O_1^{1.2.3},O_4^{4.5},O_6^{6.7},O_9^{9.10}$-nonakis(oxotungstate)(6–)

**Isomer 3** trivially called $\gamma\gamma$ or $\gamma$

$4.4',5.5',6.6',7.7',8.8',9.9'$-hexa-$\mu$-oxo-[pentadeca-$\mu$-oxo-$\mu_3$]-tetraoxophosphato(V)-$O_1^{1.2.3},O_4^{4.5},O_6^{6.7},O_9^{9.10}$-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,10f.16c,11c.12b,11f.17b,12e.13d,12f.17c,= 13c.14b,13f.18b,14e.15d,14f.18c,15f.16b,16f.17d,= 16d.18f,17f.18d-hexatungstaconta-$\mu$-oxo-$\mu_9$-[tetraoxophosphato(V)-$O_1^{1.2.3},O_4^{4.5},O_6^{6.7},O_9^{9.10}$]-nonakis(oxotungstate)(6–)

**Isomer 2**

1c.2a,1a.3c,1f.4a,1e.9a,2c.3a,2e.5a,2f.6a,3e.7a,= 3f.8a,4c.5b,4b.9c,4f.10a,5c.6b,5f.11a,6e.7d,= 6f.12a,7e.8d,7f.13a,8e.9d,8f.14a,9d.15a,10c.11b,= 10d.15e.16f,11e.12d,11f.16c,12c.13b,12f.17b,= 13e.14d,13f.18b,14e.15d,14f.18c,15f.16b,16f.17d,= 16d.18f,17f.18d-hexatungstaconta-$\mu$-oxo-$\mu_9$-[tetraoxophosphato(V)-$O_1^{1.2.3},O_4^{4.5},O_6^{6.7},O_9^{9.10}$]-nonakis(oxotungstate)(6–)

**Isomer 3**

1c.2a,1a.3c,1f.4a,1e.9a,2c.3a,2e.5a,2f.6a,3e.7a,= 3f.8a,4c.5b,4b.9c,4f.10a,5c.6b,5f.11a,6e.7d,= 6f.12a,7e.8d,7f.13a,8e.9d,8f.14a,9d.15a,10c.11b,= 10d.15e.16f,11e.12d,11f.16c,12c.13b,12f.17b,= 13e.14d,13f.18b,14e.15d,14f.18c,15f.16b,16f.17d,= 16d.18f,17f.18d-hexatungstaconta-$\mu$-oxo-$\mu_9$-[tetraoxophosphato(V)-$O_1^{1.2.3},O_4^{4.5},O_6^{6.7},O_9^{9.10}$]-nonakis(oxotungstate)(6–)

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

As it happens with the Keggin structure, or its derivatives, the Dawson structure may be degraded by taking away some tungsten atoms. For instance, one terminal group $W_3O_{13}$ may be withdrawn and the resulting pentatungstate may be used as a ligand onto a dicobalt group, yielding [Co$_4$(As$_4$O$_7$)$_2$]- (Figure 36). 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 atom, 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[1,2,3,1,3,1,4,1,2,3,2,5,2,6,3,7,3,8,4,5,4,9,4,10,= 5,6,5,11,6,7,6,12,7,8,13,9,8,14,9,15,10,11,= 10,15,11,12,13,1,14,14,1,15,heptacoarsenato-$\mu_9$-tetraoxoarsenato(V)-$O_1^{1.2.3},O_4^{4.5},O_6^{6.7},O_9^{9.10}$]-[$\mu_6$-tetraoxoarsenato(V)-$O_9^{9.10}$]-[O$_{12.13}$,O$_{14.15}$]-$\{1,2,\text{O}^\prime\}$-10,11,12,13,14,15-hexaoxo-pentadecakis(oxotungstate)(6–).
One may also think about showing the 5-fold symmetry using five times a PW$_6$O$_{14}$ group to which a name is given. Then, a series of $\mu$-oxo bridges show how they are connected.

$1,1',1',1',2,2',2',3,3',3,4,4',4',5,5',6,6'$-icosa-$\mu$-oxo-pentakis[$1.2,1.3,2.3,2.5,\ldots$]

A heteropolyanion with 5-fold symmetry has a 5-fold axis of symmetry (Figure 37). Each PW$_6$O$_{14}$ group has two such neighboring groups and it shares four oxygen atoms with each of them, so that there are 20 $\mu$-oxo bridges in the whole structure interconnecting five PW$_6$O$_{14}$ groups. The shortest name is found by counting the oxygen atoms:

1$\times$O$_{13}$, 2$\times$O$_{15}$, 2$\times$O$_{11}$, 2$\times$O$_{12}$, 1$\times$O$_{17}$, 1$\times$O$_{13}$, 2$\times$O$_{14}$ = 2$\times$O$_{15}$-dicobaltate(20$^-$).

P$_2$W$_{12}$O$_{48}$ is another fragment which can be obtained by stripping off further the Dawson compound. [P$_2$W$_{48}$O$_{166}$]-34 is named as above, using the fact that it may be considered as a ring made of four P$_2$W$_{12}$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$_3$W$_{39}$O$_{116}$]-15 is the fusion of five PW$_6$O$_{22}$ groups which are joined together, forming a doughnut-shaped compound which has a 5-fold axis of symmetry (Figure 37). Each PW$_6$O$_{22}$ group has two such neighboring groups and it shares four oxygen atoms with each of them, so that there are 20 $\mu$-oxo bridges in the whole structure interconnecting five PW$_6$O$_{14}$ groups. The shortest name is found by counting the oxygen atoms:

hexaconta-$\mu$-oxo-pentakis[$\mu_6$-
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$\times$W$_{1,1'}$, 6$\times$W$_{1,5'}$, 15$\times$W$_{2,3}$, 2$\times$W$_{2,7}$, 2$\times$W$_{2,8}$, 3$\times$W$_{3,4}$, 3$\times$W$_{3,9}$, 3$\times$W$_{3,10}$, 4$\times$W$_{4,5}$, = 41$\times$W$^{14-}$.

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 conveyed. Such abridged names still remain longer than trivial names. This is why chemists in their everyday discussions prefer to use trivial names because they 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

**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 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.

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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.

VI. References

(6) Lindqvist, I. Arkiv Kemi 1950, 2, 349.
(40) D'Amour, H.; Allman, R. Naturwissenschaften 1974, 61, 34.
(49) Dawson, B. Acta Crystallogr. 1953, 6, 113.
(51) Contant, R. Personal communication.

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