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# NOMENCLATURE OF POLYANIONS 

(Recommendations 1987)

## Prepared for publication by

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# Nomenclature of polyanions (Recommendations 1987) 


#### Abstract

PREAMBLE

A polyanion is formed by the condensation of several simple anions with the elimination of water. These negatively charged species have structures mainly made of octahedrons (polytungstates or polymolybdates), tetrahedrons (polyphosphates), and sometimes of octahedrons and tetrahedrons (polytungstates or polymolybdates). The octahedrons and tetrahedrons consist of a central atom surrounded by, respectively, six or four atoms which will be called ligands in this document. The octahedrons and tetrahedrons share edges and vertices. The structure considered as an unsubstituted parent is the one which contains oxygen atoms as ligands. Central atoms may be atoms of metals or, sometimes, non-metals. Some other rare cases of 5 -atom coordination and 7 -atom coordination are known.


Either a central atom or a ligand can be replaced. Therefore, every atomic position must be numbered, in order to be recognized and to distinguish isomers. In nomenclature of coordination compounds, lower case letters have been proposed as locant designators for vertex designation. Central atoms have not commonly been given locant designators; however, number locants have been used for numbering metal atoms in homoatomic aggregates. In the first case, the position of a ligating atom of the ligands in the coordination polyhedrons is given by a lower case letter. In the latter case, the ligand atom is indicated by a number which defines the central atom to which it is bound; if the ligand bridges several central atoms, several numbers are used. Thus, two locant systems presently coexist.

In the specific case of polyanions, difficulties arise because both central atoms and ligands can be replaced. The number of vertices of a condensed species is, in most instances, quite large: for example, [ $\left.\mathrm{SiW}_{12} \mathrm{O}_{40}\right]^{4-}$ has 40 vertices and is far from being the largest known polyanion. Obviously, the 26 letters of the alphabet are not sufficient if they are used for designating each vertex position. Since it is necessary to distinguish isomers, some sort of unambiguous designation for central atoms, as well as for vertices, has to be devised. Moreover the use of the numbers of the two central atoms is not satisfactory for designating bridging atoms because two bridges can occur between the same two central atoms.

The following numbering system is proposed:
(a) each central atoms is given a number: $1,2,3$, etc
(b) each polyhedron vertex is given a letter: octahedron $a, b, c, d, e, f$ tetrahedron $a, b, c, d$

A vertex is then designated by a number followed by a letter, the number referring to the central atom, e.g., 1a, 3d, etc. Then, when two octahedrons share a vertex, this vertex has two designations, one coming from the first octahedron, and one coming from the second octahedron, each octahedron surrounding its central atom. The designation with the lowest central atom number takes precedence. For example, if a vertex is 1 d in the first octahedron and 4 a in the second one, it is designated by 1d. 4 a . Such a multiple designation might appear unnecessarily redundant However, it may prove distinctly useful; for instance in a discussion involving ligands located at vertices 1 d and 4 f , if 4 a is an alternative for $1 \mathrm{~d}, 4 \mathrm{a}$ may be used instead of 1 d to make it quite obvious that the two vertices, 4 a and 4 f , belong to the same octahedron. Moreover, this double designation makes it quite simple to name a common vertex: e.g., 1d.4a shows that atom 1 d is also 4 a thus bridging central atoms 1 and 4 by their respective vertices $d$ and $a$.

The numbering system used in this document is consistent with the principles developed for boron cage compounds and the names are based on coordination nomenclature, not on traditional oxoanion nomenclature, e.g., tetraoxophosphate(3-) not phosphate.

## II.3.1.* NUMBERING OF CONDENSED POLYANIONS

The numbering of a condensed structure is based on the unsubstituted parent structure for the polyanion. 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 centres.

The following numbering rules are applied sequentially.

## II.3.1.1. Choice of reference axis (see Fig. 1)

(a) The reference axis is the rotational axis of the polyanion structure of highest order; it is oriented vertically.
(b) Perpendicular to the reference axis, several skeletal planes may be encountered. A 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 axis 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 rotational symmetry, the reference axis then is the axis perpendicular to the skeletal plane with the greatest number of octahedral centres.


Figure 1. Octahedron assembly and locant designators in the Lindqvist structure.

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## II.3.1.2. Choice of preferred 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 one.
(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 II.3.1.4.
(d) When a further choice is necessary, the preceding rules are applied considering the first internal skeletal planes, and so on.

## II.3.1.3. 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 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 II.3.1.4. and II.3.1.5.
(e) When a choice is left, the 12 o'clock position is chosen on a ligating atom.

## II.3.1.4. Numbering central atoms

(a) Central atoms are numbered starting from the 12 o'clock position in the preferred terminal skeletal plane and turning clockwise (or anticlockwise). 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 when starting from the 12 o'clock position, turning clockwise or anticlockwise, depending on the lowest locant requirement (see II.3.1.4.b. and II.3.1.5.).
(b) When a central atom or a ligand is substituted (see II.3.1.5.), it does not lower the symmetry of the skeleton for the choice of the reference axis of symmetry 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 IV has the smallest possible number or the earliest possible letter. Nevertheless, the choice of the first skeletal plane as defined in II.3.1.2. takes precedence over the number of a substituting central atom. When the polyanion contains several central atoms of several different atomic species, the largest number of atoms of the species coming first in Table IV will be numbered before numbering an atom coming second in Table IV, and so on.

## II.3.1.5. 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 main 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 main reference axis. The intersection with the main axis is the 12 o'clock position in the considered local skeletal plane.

Letters a, b, c, d, e, fare 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 IV of the ligand atoms occupying them. An earlier position in Table IV 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 $\mathrm{CH}_{3} \mathrm{COO}$ are considered to come immediately after oxygen and before any other element...

## II.3.2. POLYANIONS WITH SIX CENTRAL ATOMS

The first representative example of a metal polyanion with six central atoms to have its structure determined was $\mathrm{K}_{8}\left[\mathrm{Nb}_{6} \mathrm{O}_{19}\right]$ by Lindquist. The idealized structure has $O_{h}$ symmetry (figure 1). Several modifications of this structure are known:
(a) all central atoms are identical: such ions are commonly termed as isopolyanions; a better name is homopolyanions;
(b) one or more central atoms are substituted; these ions are commonly termed as mixed polyanions or heteropolyanions;
(c) some ligands are substituted.

Since substitution can occur either at a central atom or at a ligand site, these substituted ions are named in this document as heterocentre polyanions or heteroligand polyanions, respectively.

## II.3.2.1. Homopolyanions (isopolyanions)

In this structure, the metal atom has only oxygen ligands and there are six fused octahedrons; it is sufficient to count the number of oxygens of each kind, i.e., of the same coordination.

## Example <br> 1. $\left[\mathrm{Nb}_{6} \mathrm{O}_{19}\right]^{8-}$ <br> dodeca- $\mu$-oxo- $\mu_{6}$-oxo-hexaoxohexaniobate(8-)

## Example

2. $\left[\mathrm{W}_{6} \mathrm{O}_{19}\right]^{2-}$
dodeca- $\mu$-oxo- $\mu_{6}$-oxo-hexaoxohexatungstate(2-)
Multiplicative prefixes may be used to provide alternative shorter names, e.g., with equivalent NbO or WO groups:

## Example

3. $\left[\mathrm{Nb}_{6} \mathrm{O}_{19}\right]^{8-}$
dodeca- $\mu$-oxo- $\mu_{6}$-oxo-hexakis(oxoniobate)(8-)
An homopolyanion (isopolyanion) can be reduced without electron localization. Such compounds are characterized by "intervalence spectra" and are commonly termed "mixed valence compounds". The above names are used with the resulting charge expressed by the Ewens-Bassett number. For example, $\left[\mathrm{Mo}_{6} \mathrm{O}_{19}\right]^{2-}$ can be reduced into $\left[\mathrm{Mo}_{6} \mathrm{O}_{19}\right]^{3-}$ which may be named:

## Example

4. $\left[\mathrm{Mo}_{6} \mathrm{O}_{19}\right]^{3-}$
dodeca- $\mu$-oxo- $\mu_{6}$-oxo-hexakis(oxomolybdate)(3-)

However, when it is necessary to express electron localization in the reduced species, the polyanion is named in the same manner as a heterocentre polyanion. In this case, the atom with lower oxidation state comes first in the formula and precedes those with the higher valencies in the name When numbering central atoms, the lowest possible number is assigned to the reduced atom.

## II.3.2.2. Heterocentre polyanions

## II.3.2.2.1. Mono or polysubstitution

In names central atoms are cited in alphabetical order independently of the numbering scheme. The list of central atom element names is enclosed in parentheses with the ending ate after the parenthesis.

## Example

```
1. \(\left[\mathrm{NbW}_{5} \mathrm{O}_{19}\right]^{3-}\)
dodeca- \(\mu\)-oxo- \(\mu_{6}\)-oxo-hexaoxo(niobiumpentatungsten)ate(3-)
```


## Example

2. $\left[\mathrm{Nb}_{5} \mathrm{WO}_{19}\right]^{7-}$
dodeca- $\mu$-oxo- $\mu_{6}$-oxo-hexaoxo(pentaniobium-1-tungsten)ate(7-)
dodeca- $\mu$-oxo- $\mu_{6}$-oxo-hexaoxo[pentaniobium(V)-1-tungsten(VI)]ate
Tungsten is assigned number 1 because of its position in Table IV.

## Example

3. $\left[\mathrm{Nb}_{4} \mathrm{~W}_{2} \mathrm{O}_{19}\right]^{6-}$
dodeca- $\mu$-oxo- $\mu_{6}$-oxo-hexaoxo(tetraniobium-1,2-ditungsten)ate(6-)
dodeca- $\mu$-oxo- $\mu_{6}$-oxo-hexaoxo(tetraniobium-1,6-ditungsten)ate(6-)
In this example, two isomers occur and they are commonly designated cis and trans isomers. The numbering system outlined above coupled with coordination nomenclature provides a unique name for each isomer.

## Example

4. $\left[\mathrm{V}_{2} \mathrm{~W}_{4} \mathrm{O}_{19}\right]^{4-}$
dodeca- $\mu$-oxo- $\mu_{6}$-oxo-hexaoxo(tetratungsten-5,6-divanadium)ate(4-)
dodeca- $\mu$-oxo- $\mu_{6}$-oxo-hexaoxo(tetratungsten-3,5-divanadium)ate(4-)

Vanadium locants are related to vanadium position in Table IV.

## Example

5. $\left[\mathrm{NbVW}_{4} \mathrm{O}_{19}\right]^{4-}$
dodeca- $\mu$-oxo- $\mu_{6}$-oxo-hexaoxo(5-niobiumtetratungsten-3-vanadium)ate(4-)

When the substituted positions are not known, then locant designators are not given.

## Example

6. $\left[\mathrm{Nb}_{4} \mathrm{~W}_{2} \mathrm{O}_{19}\right]^{6-}$
dodeca- $\mu$-oxo- $\mu_{6}$-oxo-hexaoxo(tetraniobiumditungsten)ate(6-)

## II.3.2.2.2. Reduced heterocentre polyanions

Generally, the most easily reducible central atom is known:

## Example

1. $\left[\mathrm{Nb}_{5} \mathrm{WO}_{19}\right]^{8-}$
dodeca- $\mu$-oxo- $\mu_{6}$-oxo-hexaoxo[pentaniobium( V )tungsten $(\mathrm{V})$ ]ate
In this example, tungsten is reduced. In more complicated cases, the Ewens-Bassett number may be used.

## Example

2. $\left[\mathrm{Nb}_{4} \mathrm{~W}_{2} \mathrm{O}_{19}\right]^{7-}$
dodeca- $\mu$-oxo- $\mu_{6}$-oxo-hexaoxo(tetraniobium-1,2-ditungsten)ate(7-)
In this example, the compound has been reduced by two electrons; it is a mixed valence ion. If the electron is localized (hypothetical compound), it is possible to indicate the reduced atom by using Stock numbers.
dodeca- $\mu$-oxo- $\mu_{6}$-oxo-hexaoxo[tetraniobium( V )-1-tungsten(V)-6-tungsten(VI)]ate.

## II.3.2.3. Heteroligand polyanions

In the preceding compounds, metal atoms are surrounded by oxygen ligands. These ligands can be replaced by sulfur ligands, hydroxo ligands, etc.

## II.3.2.3.1. Single substitution

When one substitution takes place, abbreviated names without locants may be used:

## \section*{Example} <br> 1. $\left[\mathrm{W}_{6} \mathrm{O}_{18} \mathrm{~S}\right]^{2-}$

dodeca- $\mu$-oxo- $\mu_{6}$-oxo-pentaoxothiohexatungstate(2-)
undeca- $\mu$-oxo- $\mu_{6}$-oxo-hexaoxo- $\mu$-thio-hexatungstate(2-)
dodeca- $\mu$-oxo- $\mu_{6}$-oxo-pentaoxo-1a-thiohexatungstate(2-)
undeca- $\mu$-oxo- $\mu_{6}$-oxo-hexaoxo-1b- $\mu$-thio-hexatungstate(2-)

## II.3.2.3.2. Several substitutions

When two oxygen atoms of a homopolyanion (isopolyanion) are replaced, then numbering is necessary. The numbering order of central atoms may depend on the place in Table IV of the ligating atom of the replacing group.

## Example

1. $\left[\mathrm{Mo}_{6} \mathrm{O}_{17} \mathrm{~S}_{2}\right]^{2-}$
dodeca- $\mu$-oxo- $\mu_{6}$-oxo-tetraoxo-5d,6f-dithiohexamolybdate(2-)
Two terminal oxygen atoms are replaced.

## Example

2. $\left[\mathrm{W}_{6} \mathrm{O}_{17}(\mathrm{OH}) \mathrm{S}\right]^{-}$
$5 f-\mu$-hydroxo-undeca- $\mu$-oxo- $\mu_{6}$-oxo-pentaoxo-6f-thiohexatungstate(1-)

One terminal oxygen atom is replaced by a sulfur atom, and one bridging oxygen is replaced by an hydroxo group.

## Example

3. $\left[\mathrm{NbW}_{5} \mathrm{O}_{18} \mathrm{~S}\right]^{3-}$
dodeca- $\mu$-oxo- $\mu_{6}$-oxo-pentaoxo-1a-thio(6-niobiumpentatungsten)ate(3-)
Sulfur is terminal and bound to tungsten.

## Example

4. $\left[\mathrm{MO}_{6} \mathrm{O}_{17}(\mathrm{OH})_{2}\right]^{2-}$

1e,2e-di- $\mu$-hydroxo-deca- $\mu$-oxo- $\mu_{6}$-oxo-hexaoxo(1,2-dimolybdenum(V)tetramolybdenum)ate(VI)
This compound has a trivial name: molybdenum blue. It is a two electron reduced compound which has also fixed hydrogen ions.

## II.3.2.4. Names of more complicated species

## Example

```
1. [CeW (fio O
bis(octa-\mu-0\times0-\mu
```

This compound is derived from the Lindqvist structure by the loss of a tungsten atom; then two such groups are coordinated to one cerium atom.

## Example

$\begin{aligned} & \text { 2. }\left[W_{10} O_{32}\right]^{4-} \\ & \text { tetra- }- \text {-oxo-bis }\left[0 c t a-\mu-o \times o-\mu_{5}-o \times o-p e n t a k i s(o x o t u n g s t a t e)\right](4-) ~\end{aligned}$

$\left[W_{10} O_{32}\right]^{4-}$


Figure 2. Examples of polyanions derived from the Lindqvist structure.
[CeW $\left.10 \mathrm{O}_{36}\right]^{8-}$ is made of two $\mathrm{W}_{5} \mathrm{O}_{18}$ subunits with Ce joining them with an oxygen antiprism surrounding.
$\left[\mathrm{W}_{10} \mathrm{O}_{32}\right]^{4-}$ is made of two $\mathrm{W}_{5} \mathrm{O}_{18}$ subunits directly linked.
$\left[\mathrm{Mn}\left(\mathrm{Nb}_{6} \mathrm{O}_{19}\right)\left(\mathrm{Ta}_{6} \mathrm{O}_{19}\right)\right]^{12-}$ is made of two Lindqvist units linked by an Mn atom with an oxygen octahedral surrounding.

This compound has a trivial name: tungstate Y ; it is made of two identical units sharing four vertices; each unit derives from the Lindqvist structure by the loss of one tungsten atom.

## Example

3. $\left[\mathrm{MnNb}_{6} \mathrm{Ta}_{6} \mathrm{O}_{38}\right]^{12-}$
(figure 2)
[dodeca- $\mu$-oxo- $\mu_{6}$-oxo-hexakis(oxoniobato)( $8-$ )- $O^{1 \mathrm{~b}}, O^{1 \mathrm{c}}, O^{2 \mathrm{e}}$ ][dodeca- - -oxo- $\mu_{6}$-oxo-hexakis= (oxotantalato) ( $8-$ ) $-O^{1 \mathrm{~b}}, O^{1 \mathrm{c}}, \mathrm{O}^{2 e}$ ]manganate(12-)

This compound contains two Lindqvist units; each one is linked by three oxygens ligated to manganese which is octahedrally coordinated.

## II.3.3. POLYANIONS WITH THE ANDERSON STRUCTURE

## II.3.3.1. Polyanions with seven central atoms

These compounds are derived from $\left(\mathrm{NH}_{4}\right)_{6}\left[\mathrm{Mo}_{6} \mathrm{TeO}_{24}\right]$, the structure of which was proposed by Anderson and solved by Evans. The seven atoms of tellurium and molybdenum are all octahedrally surrounded and in the same plane or nearly so (figure 3). These polyanions have $D_{3 d}$ symmetry. Examples are $\left[\mathrm{Mo}_{6} \mathrm{TeO}_{24}\right]^{6-},\left[\mathrm{IMo}_{6} \mathrm{O}_{24}\right]^{5-},\left[\mathrm{H}_{6} \mathrm{CrMo}_{6} \mathrm{O}_{24}\right]^{3-}$.

The central atoms, all octahedrally surrounded, are considered equivalent and their names and symbols are cited in alphabetical order in names and formulae. The numbering of these structures is achieved by starting with the peripheral octahedrons, termed the crown, whatever the position of the central atom located at the centre of the crown is in Table IV. Thus the structural analogy between all these compounds and those where the central atom located at the centre of the crown can be removed and replaced by two tetrahedrons, one on each side of the crown, is clearly indicated (see II.3.3.2.).

## Example

$\frac{\text { Example }}{\text { 1. }\left[\mathrm{Mo}_{6} \mathrm{TeO}_{24}\right]^{6-}}$
hexa- $\mu$-oxo-hexa- $\mu_{3}$-oxo-dodecaoxo(hexamolybdenum-7-tellurium)ate(6-)


## Example

2. $\left[\mathrm{H}_{6} \mathrm{CrMo}_{6} \mathrm{O}_{24}\right]^{3-}$
hexa- $\mu_{3}$-hydroxo-hexa- $\mu$-oxo-dodecaoxo[7-chromium(III)hexamolybdenum]ate(3-)
In the preceding example, although hydrogen positions are not known, it is assumed they form hydroxo groups on the six $\mu_{3}$ bridges. If it is preferred not to show the hydrogen positions, the name should be:
hexahydrogenhexa- $\mu$-oxo-hexa- $\mu_{3}$-oxo-dodecaoxo[7-chromium(III)hexamolybdenum]ate(3-)

An isomer of this polyanion has been postulated with the chromium atom in the peripheral crown:

## Example

3. $\left[\mathrm{H}_{6} \mathrm{CrMo}_{6} \mathrm{O}_{24}\right]^{3-}$

1b, 1e-diaqua-1c,1d-di- $\mu$-hydroxo-1a,1f-di- $\mu_{3}$-hydroxo-2f,3c,4f,5c-tetra- $\mu$-oxo- $2 \mathrm{c}, 3 \mathrm{f}, 4 \mathrm{c}, 5 \mathrm{f}$-tetra- $=$ $\mu_{3}$-oxo-decaoxo[1-chromium(III)hexamolybdenum]ate

## II.3.3.2. Names of more complicated species

There are several examples of polyanions deriving from the Anderson type polyanion. Such compounds usually have $D_{3 d}$ symmetry. The structure is made of six octahedrons fused in a crown plus two tetrahedrons attached by their base on each side of the crown. These tetrahedrons share three oxygen atoms with the six octahedrons.

## Example

1. $\left[\mathrm{As}_{2} \mathrm{Mo}_{6} \mathrm{O}_{26}\right]^{6-}$
bis- $\mu_{6}$-(tetraoxoarsenato- $O, O^{\prime}, O^{\prime \prime}$ )-hexa- $\mu$-oxo-hexakis(dioxomolybdate)(6-)

## Example

```
2. \(\left[\mathrm{Mo}_{8} \mathrm{O}_{26}\right]^{4-}\)
bis- \(\mu_{6}\)-(tetraoxomolybdato- \(O, O^{\prime}, O^{\prime \prime}\) )-hexa- \(\mu\)-oxo-hexakis(dioxomolybdate)(4-)
```


## Example

3. $\left[\mathrm{Mo}_{6} \mathrm{O}_{24}\left(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{As}\right)_{2}\right]^{4-}$
bis- $\mu_{6}$-(phenylarsonato- $O, O^{\prime}, O^{\prime \prime}$ )-hexa- $\mu$-oxo-hexakis(dioxomoiybdate)(4-)
Since there are two different environments- one tetrahedral and one octahedral- and since the tetrahedral group can be replaced, it is useful to distinguish the different coordination geometries. This is accomplished by treating the tetrahedron as a ligand. It will be seen later with Keggin type polyanions another advantage of this particular treatment of tetrahedrons. Thus, for Anderson structures, the numbering of the central atoms in the crown is in no case altered by changing the tetrahedral bridging groups.

## II.3.4. POLYANIONS WITH TWELVE CENTRAL ATOMS

The structure of the anion $\left[\mathrm{PW}_{12} \mathrm{O}_{40}\right]^{3-}$ is known as the Keggin structure. Many compounds have this structure or a closely related one.

In formulae, the heteroatom such as phosphorus above, which is tetrahedrally coordinated, is cited first in order to conform with common usage in heteropolyanion chemistry. If there are several different metal atoms, they are given in alphabetical order. Finally, ligand symbols are cited as in coordination compound names.

## II.3.4.1. Compounds with the Keggin structure and isomers

## II.3.4.1.1. Compounds containing only one kind of transition metal

This family is characterized by the general formula [ $\left.X_{12} \mathrm{O}_{40}\right]^{\mathrm{n}-}$, for example, [SiW $\left.\mathrm{SiO}_{40} \mathrm{O}_{40}\right]^{4-}$ or $\left[\mathrm{PMo}_{12} \mathrm{O}_{40}\right]^{3-}$. M can be either tungsten or molybdenum; $X$ can be silicon, germanium, phosphorus, arsenic, or boron.

The polyanion is made of four $\mathrm{M}_{3} \mathrm{O}_{13}$ groups which share vertices. Such a group has a trigonal axis of symmetry and contains three octahedrons sharing edges. The three octahedrons have a common vertex which also is a vertex of the central $\mathrm{XO}_{4}$ tetrahedron. The central $\mathrm{XO}_{4}$ group is treated as a bridging ligand. The structure has $T_{d}$ symmetry (figures 4 and 5 ). In some cases, $X$ may be absent. With all the bridges designated, the name for the anion with the Keggin structure is

## Example

1. $\left[\mathrm{SiW}_{12} \mathrm{O}_{40}\right]^{4-}$

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,= $6 \mathrm{f} .11 \mathrm{~b}, 7 \mathrm{e} .8 \mathrm{~d}, 7 \mathrm{f} .11 \mathrm{c}, 8 \mathrm{c} .9 \mathrm{~b}, 8 \mathrm{f} .12 \mathrm{~b}, 9 \mathrm{f} .12 \mathrm{c}, 10 \mathrm{f} .11 \mathrm{~d}, 10 \mathrm{~d} .12 \mathrm{f}, 11 \mathrm{f} .12 \mathrm{~d}$-tetracosa- $\mu-0 \times 0-\mu_{12}$-(tetraoxo $=$ silicato- $O^{1.4 .9}, O^{2.5 .6}, O^{3.7 .8}, O^{10.11 .12}$ )-dodecakis(oxotungstate)(4-)


Five isomers are likely to occur; in the above structure one or several $\mathrm{M}_{3} \mathrm{O}_{13}$ groups can be rotated by $60^{\circ}$ around their threefold axes. This brings an additional difficulty into the nomenclature of these polyanions. Two structures are presently known as $\alpha$ and $\beta$. Alpha ( $\alpha$ ) has the Keggin structure, i.e., $T_{d}$ symmetry. Beta ( $\beta$ ) derives from a by rotating one $\mathrm{M}_{3} \mathrm{O}_{13}$ group (figures 6 and 7 ). It has $C_{3 v}$ symmetry. The third known isomer is illustrated by $\left[\mathrm{Al}_{13}\left(\mathrm{H}_{2} \mathrm{O}\right)_{12}(\mathrm{OH})_{24} \mathrm{O}_{4}\right]^{7+}$ wherein the central group is $\mathrm{AlO}_{4}$. In this compound all four groups are rotated as compared to the $\alpha$ isomer; the symmetry is $T_{d}$. The numbering of octahedral central atoms gives an unambiguous name.

## Example

2. $\left[\mathrm{SiW}_{12} \mathrm{O}_{40}\right]^{4-} \quad$ trivially called $\beta$ (figure 6)

1c.2b,1b.3c,1e.4a,1d.9a,2c.3b,2d.5a,2e.6a,3d.7a,3e.8a,4c.5b,4d.9e,4f.10c,5e.6d,5f.11b,6c.7b,= $6 \mathrm{f} .11 \mathrm{c}, 7 \mathrm{e} .8 \mathrm{~d}, 7 \mathrm{f} .12 \mathrm{~b}, 8 \mathrm{c} .9 \mathrm{~b}, 8 \mathrm{f} .12 \mathrm{c}, 9 \mathrm{f} .10 \mathrm{~b}, 10 \mathrm{f} .11 \mathrm{~d}, 10 \mathrm{~d} .12 \mathrm{f}, 11 \mathrm{f} .12 \mathrm{~d}$-tetracosa- $\mu-0 \times 0-\mu 12^{-=}=$ (tetraoxosilicato- $O^{1.4 .9}, O^{2.5 .6}, O^{3.7 .8}, O^{10.11 .12}$ )-dodecakis(oxotungstate)(4-)

In order to keep names as simple as possible, only oxygen atoms bridging skeletal planes need to be designated. These oxygen atoms are given the set of two numbers which refer to the central atoms


Figure 6. Octahedron assembly and locant designators in isomer 2 deriving from isomer 1 (Keggin structure) by rotating one $\mathrm{W}_{3} \mathrm{O}_{13}$ group by $60^{\circ}$. This isomer, sometimes trivially called $\beta$, has $C_{3 v}$ symmetry.


Figure 7. Two dimensional opened isomer structures with the formula $\mathrm{XW}_{12} \mathrm{O}_{40}$. Black points are central atoms. A single line between two central atoms means a common octahedral vertex. A double line between two central atoms means a shared octahedral edge. Doubly underlined numbers refer to the isomer number in text.
joined by the considered oxygen atoms. This results in the following sequence of numbers for the bridging oxygens which differentiate quite clearly the five isomers (see figure 7).

- the basic isomer of Keggin structure : $\alpha$-isomer 1
$1.4,1.9,2.5,2.6,3.7,3.8,4.10,5.10, .6 .11,7.11,8.12,9.12$
- one $\mathrm{M}_{3} \mathrm{O}_{13}$ group is rotated by $60^{\circ}: \beta$-isomer 2
$1.4,1.9,2.5,2.6,3.7,3.8,4.10,5.11,6.11,7.11,8.12,9.10$
- two $\mathrm{M}_{3} \mathrm{O}_{13}$ groups are rotated by $60^{\circ}: \gamma$-isomer 3
$1.3,1.6,2.4,2.5,3.7,3.9,4.7,4.10,5.8,5.11,6.8,6.12,7.9,7.10,8.11,8.12$
- three $\mathrm{M}_{3} \mathrm{O}_{13}$ groups are rotated by $60^{\circ}$ : $\delta$-isomer 4
$1.4,1.6,2.4,2.5,3.5,3.6,4.7,4.8,5.9,5.10,6.11,6.12$
- four $\mathrm{M}_{3} \mathrm{O}_{13}$ groups are rotated by $60^{\circ}$ : $\mathrm{Al}_{13}$ cation : $\varepsilon$-isomer 5
1.4,1.4,2.5,2.5,3.6,3.6,4.7,4.12,5.8,5.9,6.10,6.11


## Example

3. $\left[\mathrm{SiW}_{12} \mathrm{O}_{4 \mathrm{O}}\right]^{4-} \quad$ Keggin structure
1.4,1.9,2.5,2.6,3.7,3.8,4.10,5.10,6.11,7.11,8.12,9.12-dodeca- - -oxo- $\mu_{12}$-(tetraoxosilicato-= $O^{1.4 .9}, O^{2.5 .6}, O^{3.7 .8}, O^{10.11 .12}$ )-tetrakis[tri- $\mu$-oxo-tris(oxotungstate)](4-)

## Example

4. $\left[\mathrm{SiW}_{12} \mathrm{O}_{4 \mathrm{O}}\right]^{4-} \quad$ one $\mathrm{M}_{3} \mathrm{O}_{13}$ group rotated
1.4,1.9,2.5,2.6,3.7,3.8,4.10,5.11,6.11,7.12,8.12,9.10-dodeca- - -oxo- $\mu_{12}$-(tetraoxosilicato-= $o^{1.4 .9}, o^{2.5 .6}, o^{3.7 .8}, o^{10.11 .12}$ )-tetrakis[tri- $\mu$-oxo-tris(oxotungstate)](4-)

## Example

5. $\left[\mathrm{Al}_{13} \mathrm{O}_{4} \mathrm{O}_{48}\right]^{7+} \quad$ (figure 7)
1.4,1.4,2.5,2.5,3.6,4.7,4.12,5.8,5.9,6.10,6.11-dodeca- $\mu$-hydroxo- $\mu_{12}$-(tetraoxoaluminato- $=$ $0^{1.2 .3}, o^{4.7 .12}, O^{5.8 .9}, O^{6.10 .11}$ )-tetrakis[tri- $\mu$-hydroxo-tris(aquaaluminium)](7+)

Trivial nomenclature has developped in an anarchic manner for polytungstates. For example, metatungstate is a dodecatungstate of the same structure as $\alpha-\left[\mathrm{SiW}_{12} \mathrm{O}_{40}\right]^{4-}$ in which two hydrogen ions are trapped in the central cavity in the place of the silicon atom. Polytungstate $X$ is the $\beta$ isomer of the preceding metatungstate while tungstate Y is a decatungstate deriving from the Lindquist structure (see II.3.2.4).

## Example

6. $\left[\mathrm{H}_{2} \mathrm{~W}_{12} \mathrm{O}_{40}\right]^{6-} \quad$ Metatungstate
di- $\mu_{3}$-hydroxo-1.4,1.9,2.5,2.6,3.7,3.8,4.10,5.10,6.11,7.11,8.12,9.12-dodeca- $\mu$-oxo-di- $\mu_{3}$-oxo-= tetrakis[tri- $\mu$-oxo-tris(oxotungstate)](6-)

## Example

7. $\left[\mathrm{H}_{2} \mathrm{~W}_{12} \mathrm{O}_{40}\right]^{6-} \quad$ Polytungstate $X$
di- $\mu_{3}$-hydroxo-1.4,1.9,2.5,2.6,3.7,3.8,4.10,5.11,6.11,7.12,8.12,9.10-dodeca- $\mu$-oxo-di- $\mu_{3}$-oxo-= tetrakis[tri- $\mu$-oxo-tris(oxotungstate)](6-)

## II.3.4.1.2. Compounds with several transition metals, i.e. substituted compounds

This class contains many more compounds than the preceding one. Indeed the tetrahedrally surrounded atom can be substituted as well as one or several tungsten atoms. For instance, the following species (ignoring the charge) are known with the following substitutions.

$$
\begin{aligned}
& \mathrm{SiW}_{11} \mathrm{ZO}_{40} \\
& \mathrm{Z}=\mathrm{Cu}{ }^{\prime \prime}, \mathrm{Zn}^{I \prime}, \mathrm{Mn}^{\prime \prime}, \mathrm{Co}^{\prime \prime}, \mathrm{Ni}^{\prime \prime}, \mathrm{Fe}^{\prime \prime}, \mathrm{Mn}^{\text {III }}, \mathrm{Co}^{\text {III }}, \mathrm{Fe}^{\mathrm{III}}, \mathrm{Cr}^{\mathrm{III}}, \mathrm{Al}^{\text {III }} \\
& \mathrm{SiW}_{10} \mathrm{Z}_{2} \mathrm{O}_{40} \quad \mathrm{SiW}_{10} \mathrm{ZZ}^{\prime} \mathrm{O}_{40}
\end{aligned}
$$

$$
\begin{aligned}
& \mathrm{SiW}_{9} \mathrm{Z}_{3} \mathrm{O}_{40} \text { or } \mathrm{SiW}_{9} \mathrm{Z}_{2} \mathrm{Z}^{\prime} \mathrm{O}_{40} \text { or } \mathrm{SiW}_{9} \mathrm{ZZ}^{\prime} \mathrm{Z}^{\prime \prime} \mathrm{O}_{40} \\
& Z=Z^{\prime}=Z^{\prime \prime}=M \mathrm{MI}^{\mathrm{VI}}, \mathrm{~V}^{\mathrm{V}}, \mathrm{~V}^{I V}, \mathrm{Co}^{I I}, \mathrm{Mn}^{\text {III }}, \mathrm{Fe}^{\text {III }}
\end{aligned}
$$

1. Monosubstituted compounds:

The choice of the reference axis and the reference plane is governed by the rules given earlier; the hierarchy is: one, the symmetry of the idealized polyanion framework; two, the position of the substituting atom in Table IV with respect to other central atoms.

## Example

1. $\left[\mathrm{SiMoW}_{11} \mathrm{O}_{40}\right]^{4-} \quad$ trivially referred to as $\alpha$
1.4,1.9,2.5,2.6,3.7,3.8,4.10,5.10,6.11,7.11,8.12,9.12-tetracosa- $\mu$-oxo-dodecaoxo- $\mu_{12}$-(tetraoxo $=$ silicato- $\left.O^{1.4 .9}, O^{2.5 .6}, O^{3.7 .8}, O^{10.11 .12}\right)$-(1-molybdenumundecatungsten)ate(6-)

## Example

2. $\left[\mathrm{SiCoW}_{11} \mathrm{O}_{39}\left(\mathrm{H}_{2} \mathrm{O}\right)\right]^{6-} \quad$ trivially referred to as $\beta$
la-aqua-1.4,1.9,2.5,2.6,3.7,3.8,4.10,5.10,6.11,7.11,8.12,9.12-tetracosa- $\mu$-oxo-undecaoxo- $\mu_{12}=$ (tetraoxosilicato- $O^{1.4 .9}, O^{2.5 .6}, O^{3.7 .8}, O^{10.11 .12}$ )-(1-cobaltundecatungsten) ate(6-)

## Example

3. $\left[\mathrm{SiNbW}_{11} \mathrm{O}_{40}\right]^{5-} \quad$ trivially referred to as $\alpha$
$1.4,1.9,2.5,2.6,3.7,3.8,4.10,5.10,6.11,7.11,8.12,9.12$-tetracosa- $\mu$-oxo-dodecaoxo- $\mu_{12}$-(tetraoxo $=$ silicato- $O^{1.4 .9}, O^{2.5 .6}, O^{3.7 .8}, O^{10.11 .12}$ )-(12-niobiumundecatungsten) ate(5-)

For the $\beta$ structure, three isomers are likely to occur. They are trivially designated as $\beta_{1}, \beta_{2}$, and $\beta_{3}$ depending on the position of the substituted atom whether it is located on the farthest position to the rotated group, on an adjacent position to the rotated group, on an atom of the rotated group, respectively.

## Example

4. [SiVW $\left.{ }_{11} \mathrm{O}_{40}\right]^{5-} \quad$ trivially referred to as $\beta_{1}$
1.4,1.9,2.5,2.6,3.7,3.8,4.10,5.11,6.11,7.12,8.12,9.10-tetracosa- $\mu$-oxo-dodecaoxo- $\mu_{12}$-(tetraoxo $=$ silicato- $O^{1.4 .9}, O^{2.5 .6}, O^{3.7 .8}, O^{10.11 .12}$ )-(undecatungsten-3-vanadium)ate(5-)

In this example, the reference axis is of course the $C_{3}$ axis which is the axis around which the $\mathrm{M}_{3} \mathrm{O}_{13}$ group has turned. The preferred terminal skeletal plane is the less condensed one, even though it contains the vanadium atom which comes after tungsten in Table IV (see II.3.1.4.b). The reference symmetry plane is chosen to give the lowest locants to tungsten, i.e., to give the number 3 to vanadium.

## Example

5. $\left[\mathrm{SiVW}_{11} \mathrm{O}_{40}\right]^{5-} \quad$ trivially referred to as $\beta_{3}$
$1.4,1.9,2.5,2.6,3.7,3.8,4.10,5.11,6.11,7.12,8.12,9.10$-tetracosa- $\mu$-oxo-dodecaoxo- $\mu_{12}$-(tetraoxo $=$ silicato- $O^{1.4 .9}, O^{2.5 .6}, O^{3.7 .8}, O^{10.11 .12}$ )-(undecatungsten-12-vanadium)ate(5-)

## Example

6. $\left[\mathrm{SiVW}_{11} \mathrm{O}_{40}\right]^{5-} \quad$ trivially referred to as $\beta_{2}$
1.4,1.9,2.5,2.6,3.7,3.8,4.10,5.11,6.11,7.12,8.12,9.10-tetracosa- $\mu$-oxo-dodecaoxo- $\mu_{12}$-(tetraoxo $=$ silicato- $O^{1.4 .9}, O^{2.5 .6}, O^{3.7 .8}, O^{10.11 .12}$-(undecatungsten-9-vanadium) ate(5-)

Enantiomeric structures occur for this compound.
Rules can be applied to larger compounds. For instance, $\left[\mathrm{SiFeW}_{11} \mathrm{O}_{39}(\mathrm{OH})\right]^{6-}$ can dimerize yielding [ $\left.\mathrm{SiW}_{11} \mathrm{O}_{39} \mathrm{Fe}-\mathrm{O}-\mathrm{FeSiW} \mathrm{Si}_{11} \mathrm{O}_{39}\right]^{12-}$ each $\mathrm{FeW}_{11}$ unit of which has $T_{d}$ symmetry.

## Example

7. $\left[\mathrm{SiW}_{11} \mathrm{O}_{39} \mathrm{FeOFeSiW} 11 \mathrm{O}_{39}\right]^{12-}$
la- $\mu$-oxo-bis[1.4,1.9,2.5,2.6,3.7,3.8,4.10,5.10,6.11,7.11,8.12,9.12-tetracosa- $\mu$-oxo-undecaoxo= $-\mu_{12}$-(tetraoxosilicato- $O^{1.4 .9}, O^{2.5 .6}, O^{3.7 .8}, O^{10.11 .12}$ ) (1-ironundecatungsten)]ate(12-)
8. Disubstituted and polysubstituted compounds :

The proposed numbering system provides a solution to the problem of distinguishing isomers of diand poly-substituted compounds. For example, $\left[\mathrm{PMo}_{10} \mathrm{~V}_{2} \mathrm{O}_{40}\right]^{5-}$ has five isomers. Because of its position in Table IV, one vanadium must be given the locant 12 in the metal framework with $T_{d}$ symmetry. The isomers are now distinguished by the locant numbers of vanadium.

12 and $11 \quad 12$ and $8 \quad 12$ and $7 \quad 12$ and $3 \quad 12$ and 2
A trisubstituted compound containing two molybdenum atoms and one vanadium atom has been prepared. The locant 1 is given to the atom coming first in Table IV, i.e., molybdenum, and a locant number as high as possible is then given to the atom coming last, i.e., vanadium.

## Example

8. $\left[\mathrm{SiMo}_{2} \mathrm{VW}_{9} \mathrm{O}_{40}\right]^{5-}$
$1.4,1.9,2.5,2.6,3.7,3.8,4.10,5.10,6.11,7.11,8.12,9.12$-tetracosa- $\mu$-oxo-dodecaoxo- $\mu_{12}$-(tetraoxo= silicato- $\left.O^{1.4 .9}, O^{2.5 .6}, O^{3.7 .8}, O^{10.11 .12}\right)$-[1,2-dimolybdenum $(\mathrm{VI})$ nonatungsten $(\mathrm{VI})$-3-vanadium $\left.(\mathrm{V})\right]=$ ate(5-)

## II.3.4.1.3. Ligand substitution

When a ligand is substituted, the same procedure can be applied using locant designators. The anions $\left[\mathrm{HW}_{12} \mathrm{~F}_{2} \mathrm{O}_{38}\right]^{5-},\left[\mathrm{H}_{2} \mathrm{~W}_{12} \mathrm{~F}_{2} \mathrm{O}_{38}\right]^{4-},\left[\mathrm{HW}_{12} \mathrm{~F}_{3} \mathrm{O}_{37}\right]^{4-}$ are known examples where, in every case, the hydrogen ion(s) is(are) trapped in the central cavity, and where fluorine atoms always bridge three tungsten atoms.

## Example

1. $\left[\mathrm{HW}_{12} \mathrm{~F}_{2} \mathrm{O}_{38}\right]^{5-}$
$\mu_{3}$-(hydrogenfluoride)- $\mu_{3}$-fluoro-1.4,1.9,2.5,2.6,3.7,3.8,4.10,5.10,6.11,7.11,8.12,9.10-dodeca= - $\mu$-oxo-di- $\mu_{3}$-oxo-tetrakis[tri- $\mu$-oxo-tris(oxotungstate)](4-)

## II.3.4.1.4. Reduced compounds

A reduced compound is treated in the same manner as a substituted compound if the electrons coming from the redox process are localized. However, in many cases, the hopping process makes localization impossible. Then only the overall charge is changed :

## Example

1. $\left[\mathrm{SiMo}_{12} \mathrm{O}_{40}\right]^{4-}$ can be reduced by 4 electrons to give $\left[\mathrm{SiMo}_{12} \mathrm{O}_{40}\right]^{8-}$
1.4,1.9,2.5,2.6,3.7,3.8,4.10,5.10,6.11,7.11,8.12,9.12-dodeca- $\mu-$ oxo- $\mu_{12}$-(tetraoxosilicato $=$ $-O^{1.4 .9}, O^{2.5 .6}, O^{3.7 .8}, O^{10.11 .12}$ )-tetrakis[tri- $\mu$-oxo-tris(oxomolybdate)](8-)

For $\left[\mathrm{SiMo}_{2} \mathrm{~W}_{10} \mathrm{O}_{40}\right]^{6-}$, it has been shown that both electrons are localized on molybdenum atoms:

## Example

2. $\left[\mathrm{SiMo}_{2} \mathrm{~W}_{10} \mathrm{O}_{40}\right]^{6-}$
1.4,1.9,2.5,2.6,3.7,3.8,4.10,5.10,6.11,7.11,8.12,9.12-tetracosa- $\mu$-oxo-dodecaoxo- $\mu_{12-(\text { tetraoxo }=}$ silicato- $O^{1.4 .9}, O^{2.5 .6}, O^{3.7 .8}, O^{10.11 .12}$ )[1,2-dimolybdenum( V )decatungsten(VI)]ate(6-)

## II.3.4.2. Compounds in which central atoms are missing (defect structures)

Several polyanions have been prepared which can be described from the Keggin structure by removing tungsten atoms and their associated non-bridging oxygen atoms.

## II.3.4.2.1. Compounds with one vacancy

For numbering central atoms, the rules given earlier are used: the upper skeletal plane is the plane with the lowest number of central atoms, i.e., the one with the vacant position, and with the less condensed octahedrons.

Herein several possibilities can occur because there are three ways to locate the vacant position with respect to the 12 o'clock position. With the upper skeletal plane consisting of only tungsten atoms, the three possibilities are represented in the following sketch which shows the uppermost skeletal plane.

| 12 o'clock <br> $*$ | 12 o'clock <br> $\mathrm{W}_{1}$ | 12 o'clock <br> $\mathrm{W}_{1}$ |  |
| :---: | :---: | :---: | :---: |
| $\mathrm{~W}_{2}$ | $\mathrm{~W}_{1}$ | $\mathrm{~W}_{2}$ | $*$ |$\quad * \quad$| $\mathrm{W}_{2}$ |
| :--- |

The asterisk represents the vacant site. The rule to locate the vacancy is: "the vacant site is considered as an atom position and then numbered; it is given the lowest possible number". Then the choice is :

$$
\begin{gathered}
12 \text { o'clock } \\
\mathrm{W}_{2} \quad \mathrm{~W}_{1}
\end{gathered}
$$

## Example

1. $\left[\mathrm{SiW}_{11} \mathrm{O}_{39}\right]^{8-} \quad$ deriving from the Keggin structure

1c.2b,1d.4a,1e.5a,2d.6a,2e.7a,3c.4b,3d.8e,3f.9b,4e.5d,4f.9c,5c.6b,5f.10b,6e.7d,6f.10c,7c.8b,= $7 \mathrm{f} .11 \mathrm{~b}, 8 \mathrm{f} .11 \mathrm{c}, 9 \mathrm{f} .10 \mathrm{~d}, 9 \mathrm{~d} .11 \mathrm{f}, 1$ of.11d-icosa- $\mu$-oxo-pentadecaoxo- $\mu_{11}$-(tetraoxosilicato- $O^{1.4 .5}$,= $o^{2.6 .7}, o^{3.8}, o^{9.10 .11}$ )-undecatungstate(8-)

From the $\mathrm{C}_{3 v}$ isomer deriving from the Keggin structure, three isomers can be obtained by removing one central atom. The choice of the reference axis takes precedence on any other choice, i.e., wherever the vacancy is.

In the following example, the central atom is removed from the rotated $\mathrm{M}_{3} \mathrm{O}_{13}$ group.

## Example

2. $\left[\mathrm{SiW}_{11} \mathrm{O}_{39}\right]^{8-}$

1c.2a, 1e.4a, 1f.5a,2e.6a,2f.7a,3e.4d,3b.8c,3f.9c,4c.5b,4f.10b,5e.6d,5f.10b,6c.7b, 6f.11b,7e.8d, = $7 \mathrm{f} .11 \mathrm{c}, 8 \mathrm{f} .9 \mathrm{~b}, 9 \mathrm{e} .10 \mathrm{~d}, 9 \mathrm{~d} .11 \mathrm{e}, 10 \mathrm{e} .11 \mathrm{~d}$-icosa- $\mu$-oxo-pentadecaoxo- $\mu_{11}$-(tetraoxosilicato- $0^{1.2}, 0^{3.8 .9}$,= $O^{4.5 .10}, O^{6.7 .11}$ )-undecatungstate(8-)

In the following example, the central atom is removed from the plane containing six central atoms. From the rule above, the 12 o'clock position is defined with the vacant position. There are two optical isomers of this structure. As in the general practice, they have the same name; the numbering indicates chirality clockwise or anticlockwise depending on the isomer.

## Example

3. $\left[\mathrm{SiW}_{11} \mathrm{O}_{39}\right]^{8-}$

1b.3c,1c.2b,1d.8a,2c.3b,2d.4a,2e.5a,3d.6a,3e.7a,4e.5d,4f.10b,5c.6b,5f.10c,6e.7d,6f.11b,7c.8b,= $7 \mathrm{f} .11 \mathrm{c}, 8 \mathrm{f} .9 \mathrm{~b}, 9 \mathrm{~d} .11 \mathrm{f}, 9 \mathrm{f} .10 \mathrm{~d}, 10 \mathrm{f} .11 \mathrm{~d}$-icosa- $\mu$-oxo-pentadecaoxo- $\mu_{11^{-(t e t r a o x o s i l i c a t o-~} O^{1.8}, O^{2.4 .5},=}$ $O^{3.6 .7}, o^{9.10 .11}$ )-undecatungstate(8-)

In this example, the central atom is removed from the plane opposite to the plane of the rotated group.

## Example

Example
$4 . \quad\left[\mathrm{SiW}_{11} \mathrm{O}_{39}\right]^{8-}$
1c.2b,1d.4a,1e.5a,2d.6a,2e.7a,3c.4b,3d.8e,3f.9c,4e.5d,4f.10b,5c.6b,5f.10c,6e.7d,6f.11b,7c.8b,= $7 \mathrm{f} 11 \mathrm{c},. 8 \mathrm{f} .9 \mathrm{~b}, 9 \mathrm{f} .10 \mathrm{~d}, 10 \mathrm{f} .11 \mathrm{~d}, 9 \mathrm{~d} .11 \mathrm{f}$-icosa- $\mu$-oxo-pentadecaoxo- $\mu_{11}$-(tetraoxosilicato- $0^{1.4 .5}, 0^{2.6 .7},=$ $O^{3.8}, O^{9.10 .11}$ )-undecatungstate(8-)

## II.3.4.2.2. Compounds with three vacancies

Two types are known; in the first one, a complete $\mathrm{W}_{3} \mathrm{O}_{13}$ group has been removed (trivially named $B$ type) while, in the second one, three adjacent metal atoms belonging to three different $\mathrm{W}_{3} \mathrm{O}_{13}$ groups have been taken away (trivially named A type). In each case one remaining $\mathrm{M}_{3} \mathrm{O}_{13}$ group can be rotated by $60^{\circ}$.
$\begin{array}{ll}\frac{\text { Example }}{1 .}\left[\mathrm{PMo}_{9} \mathrm{O}_{28}(\mathrm{OH})_{6}\right]^{3-} & \begin{array}{l}\text { Type A deriving from } T_{d} \text { Keggin structure } \\ \text { (figure 8-I) }\end{array}\end{array}$
4f, $5 \mathrm{f}, 6 \mathrm{f}, 7 \mathrm{f}, 8 \mathrm{f}, 9 \mathrm{f}$-hexahydroxo-1c.2a,1a.3c,1f.4a,1e.9a,2c.3a,2e.5a,2f.6a,3e.7a,3f.8a, 4c.5b,4d.9e,= $5 e .6 \mathrm{~d}, 5 \mathrm{~b} .7 \mathrm{~b}, 7 \mathrm{e} .8 \mathrm{~d}, 8 \mathrm{c} .9 \mathrm{~b}$-pentadeca- $\mu-0 \times 0-\mu_{9}$ [tetraoxophosphato(V)- $\left.0^{1.2 .3}, 0^{4.5}, 0^{6.7}, 0^{8.9}\right]$-nonakis $=$ (oxomolybdate)(3-)


Figure 8. Two dimensional opened structures with formula $X M_{9} O_{n}$. Black points are central atoms. A single line refers to a shared octahedral vertex. A double line refers to a shared octahedral edge.

## Example

2. $\left[\mathrm{SiW}_{9} \mathrm{O}_{34}\right]^{10-}$

Type $A$ deriving from $C_{3 v}$ Keggin structure
(figure 8-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- $\mu$-oxo-pentadecaoxo- $\mu_{9}$ (tetraoxosilicato- $0^{1.2 .3}, 0^{4.9}, 0^{5.6}, 0^{7.8}$ )-nonatungstate(10-)

## Example

3. $\left[\mathrm{As}^{I I I} \mathrm{~W}_{9} \mathrm{O}_{33}\right]^{9-} \quad$ Type B deriving from $T_{d}$ Keggin structure
(figure 8-III)
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.8b-penta= deca- $\mu$-oxo-pentadecaoxo- $\mu_{9}$-[trioxoarsenato(III)- $O^{1.4 .9}, o^{2.5 .6}, o^{3.7 .8}$ ]-nonatungstate(9-)

## Example

4. $\left[\mathrm{As}{ }^{I I I} \mathrm{Mo}_{9} \mathrm{O}_{33}\right]^{9-} \quad$ Type $B$ deriving from $C_{3 v}$ Keggin structure
(figure 8-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-penta=de
ca- $\mu$-oxo-pentadecaoxo- $\mu_{9}$-[trioxoarsenato(III)- $O^{1.2 .3}, O^{4.6 .7}, O^{5.8 .9}$ ]-nonamolybdate(9-)

This isomer is as yet unknown.

## II.3.5. POLYANIONS WITH EIGHTEEN CENTRAL ATOMS

Another class of polyanions contains eighteen central atoms. The basic structure is known as the Dawson structure. It has $D_{3 h}$ symmetry (figure 9). Examples are $\left[\mathrm{P}_{2} \mathrm{~W}_{18} \mathrm{O}_{62}\right]^{6-},\left[\mathrm{P}_{2} \mathrm{Mo}_{18} \mathrm{O}_{62}\right]^{6-}$, $\left[\mathrm{As}_{2} \mathrm{~W}_{18} \mathrm{O}_{62}\right]^{6-},\left[\mathrm{As}_{2} \mathrm{Mo}_{18} \mathrm{O}_{62}\right]^{6-}$.

These compounds are dimers of $\mathrm{XM}_{9}$ which derive from the Keggin structure $\mathrm{XM}_{12}$. Three tungsten atoms are removed, each from a different $\mathrm{M}_{3} \mathrm{O}_{13}$ group. The $\mathrm{XM}_{9}$ units are joined together by sharing octahedral vertices. The internal $\mathrm{XO}_{4}$ tetrahedron has a basal plane towards the open side of the $\mathrm{XW}_{9}$ moiety.

The $X_{2} \mathrm{M}_{18}$ compound can be named as a complete unit using rules given earlier. The upper skeletal plane is a $\mathrm{M}_{3} \mathrm{O}_{13}$ group. Since there are two identical terminal planes, the upper one and/or the lower one, and since it has been seen previously that such a group may be rotated by $60^{\circ}$, three isomers are likely to occur; among them two are known.

Isomer 1 Uppermost skeletal plane not rotated Lowest skeletal plane not rotated

Isomer 2 Uppermost skeletal plane not rotated Lowest skeletal plane rotated

Isomer 3 Uppermost skeletal plane rotated Lowest skeletal plane rotated

For these three cases, the locant sequences of the $\mu$-oxo bridges are as follows :
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,16f.18c,15f.16b,= 16f.17d,16d.18f,17f.18d

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,10f.16b,11e.12d,11f.16c,= 12c.13b,12f.17b,13e.14d,13f.17c,14c.15b,14f.18b,15f.18c,= 1,6f.17d,16d.18f,17f.18d


Figure 9. Octahedron assembly and locant designators for the ion $\mathrm{X}_{2} \mathrm{M}_{18} \mathrm{O}_{62}$ made of two $X_{9}$ subunits.

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, 9 f.15a,10c.11b,10d.15e,10f.16c,11e.12d,11f.17b,= 12c.13b,12f.17c,13e.14d,13f.18b,14c.15b,14f.18c,15f.16b,= 16f.17d,16d.18f,17f.18d

The bold locants are the first ones to distinguish isomer 2 and isomer 3 from isomer 1 ; the underlined locants are the first ones to distinguish isomer 3 and isomer 1 from isomer 2.

## Example

1. $\left[\mathrm{P}_{2} W_{18} \mathrm{O}_{62}\right]^{6-} \quad$ 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,16f.18c,15f.16b,16f.17d,16d.18f,17f.18d-hexatriaconta= $-\mu$-oxo- $\mu_{9^{-}}$(tetraoxophosphato- $O^{1.2 .3}, O^{4.5}, O^{6.7}, O^{8.9}$ )- $\mu_{9}$-(tetraoxophosphato-= $O^{10.11}, O^{12.13}, O^{14.15}, O^{16.17 .18}$ )-octadecakis(oxotungstate)(6-)

In order to have more compact names, multiplicative prefixes can be used when the polyanion is symmetrical. It must be pointed out hat, since the polyanion has a symmetry plane perpendicular to the reference axis, the numbering is valid only for the first moiety.

## Example

2. $\left[\mathrm{P}_{2} \mathrm{~W}_{18} \mathrm{O}_{62}\right]^{6-} \quad$ isomer 1
4.10,5.11,6.12,7.13,8.14,9.15-hexa- $\mu$-oxo-bis[1c.2a,1a.3c,1f.4a,1e.9a,2c.3a,2e.5a,2f.6a,3e.7a,= 3f. $8 \mathrm{a}, 4 \mathrm{c} .5 \mathrm{~b}, 4 \mathrm{~d} .9 \mathrm{e}, 5 \mathrm{e} .6 \mathrm{~d}, 6 \mathrm{c} .7 \mathrm{~b}, 7 \mathrm{e} .8 \mathrm{~d}, 8 \mathrm{c} .9 \mathrm{~b}-$ pentadeca- $\mu-0 \times 0-\mu_{9}$-(tetraoxophosphato- $0^{1.2 .3}, 0^{4.5},=$ $O^{6.7}, O^{8.9}$ )-nonakis(oxotungstate)](6-)

## II.3.6. FINAL REMARKS

From what precedes, it appears that the names given to polyanions are complicated and carry a long sequence of numbers and letters. However, these names inevitably arise from the structural complexity of the polyanions themselves. Evidently their use in everyday practice may become tedious. If a shorter name is desired, it is always possible to consult the chapter on oxoanions of the Nomenclature of Inorganic Chemistry (last edition, Butterworths, 1970; new edition, in preparation); it is shown in this chapter how to give a name to an oxoanion of a given formula but of an unknown structure. Also, in published litterature, it is commonly accepted to use an abbreviated name provided it is clearly defined at the outset; the fully systematic name is then given once and for all in extenso somewhere in the text.

The names provided in this chapter have the merit of being systematic, in other words they allow to retrieve the structure from the name without ambiguity. The derived rules are aimed to tackle with all possible future developments in this area.


[^0]:    * The membership of the Commission during the preparation of these recommendations (19731985) was as follows:

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[^2]:    * The section numbering used is in conformity with the 3rd edition of the IUPAC 'red book' Nomenclature of Inorganic Chemistry -I to be published in 1988 by Blackwell Scientific Publications Ltd., Oxford, UK.

