

**CHEMICAL  
DATA  
SERIES**

# MOLYBDENUM CHEMICALS

Bulletin Cdb-12

October 1956

## PROPERTIES OF HETEROPOLYMOYBDATES

The heteropolymolybdates are an unusually large family of salts and free acids, each member containing a complex and high-weight anion. These heteropoly anions contain two to eighteen hexavalent molybdenum atoms around one or more hetero atoms. They are all highly oxygenated. Examples are  $[\text{PMo}_{12}\text{O}_{40}]^{-3}$ ,  $[\text{Fe}_2\text{Mo}_{12}\text{O}_{42}]^{-6}$ ,  $[\text{As}_2\text{Mo}_{18}\text{O}_{62}]^{-6}$ , and  $[\text{TeMo}_6\text{O}_{24}]^{-6}$ , where P, Fe, As, and Te are the hetero atoms.

Approximately 25 different elements have been reported to function as hetero atoms in distinct heteropolymolybdate anions. Moreover, many of these elements can act as hetero atoms in more than one series of heteropolymolybdates. Thus  $\text{P}^{+5}$  probably occurs in six distinct, stable species and  $\text{P}^{+3}$  occurs in at least two others. The total number of possible acids and salts is obviously great.

### TYPICAL PROPERTIES

Many heteropolymolybdates fall into distinct series with properties that differ somewhat from one series to another. However, the heteropolymolybdates as a class show the following general properties:

1. Heteropolymolybdates generally have very high molecular weights for inorganic electrolytes, ranging up to over 3000.
2. Free acids and most salts of heteropolymolybdate anions are extraordinarily soluble in water and are often very soluble in organic solvents as well.

**In Water:** The free acids are generally extremely soluble (up to 85% by weight of solution).

In general, the heteropolymolybdate salts of small cations, including those of many heavy metals, are also very soluble. Usually the larger the cation, the less soluble its salt with a given heteropolymolybdate anion. Cs, Ag, Hg, Pb and the larger alkaline earth salts are often insoluble. The  $\text{NH}_4$ , K, and Rb salts of some of the most important heteropolymolybdate anions are insoluble, but these three cations form other soluble heteropolymolybdate salts.

Salts of heteropolymolybdate anions with cationic coordination complexes, alkaloids, or organic amines are usually insoluble. The albumins are coagulated and precipitated by most heteropolymolybdates.

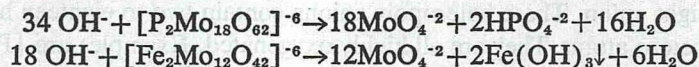
**In organic solvents:** Many of the free acids and a few of the salts are very soluble in organic solvents, especially if the latter contain oxygen. Ethers, alcohols, and ketones, in that order, are generally the best solvents. The dehydrated salts sometimes dissolve readily in organic solvents when the hydrated salts will not.

3. The crystalline free acids and salts of heteropolymolybdate anions are almost always highly hydrated. A given acid or salt will often form several solid hydrates.
4. Many heteropolymolybdates are highly colored. The colors range through the spectrum and occur in many shades. Other compounds are colorless.
5. Some heteropolymolybdates are strong oxidizing agents and can be very readily changed to fairly stable reduced heteropolymolybdates. The reduction products are colored an intense, deep blue. In solution the blue substances obey Beer's Law of light absorption. The reduced products can in turn act as reducing agents, and the original colors of the anions are restored on oxidation.

6. **The free heteropolymolybdic acids are fairly strong acids.** Dissociation constants are usually in the range  $10^{-1}$  to  $10^{-3}$ . The acids are nearly always stronger than either molybdic acid or the simple acid containing the hetero atom in corresponding oxidation state.

The free acids generally have several replaceable hydrogen ions. Accordingly, numerous crystalline acid salts have been isolated. The several replaceable hydrogen ions of the acid are typically fairly strong and differ little in dissociation constant. Neutralization of successive hydrogen ions therefore proceeds simultaneously when hydroxyl ion is added to the solution, and breaks between successive hydrogen ions are not usually detectable in the neutralization curves. (Such curves generally show breaks corresponding to the beginning and end of degradation reactions of the complex anion by hydroxyl ion. However, these breaks usually occur after neutralization of the replaceable hydrogen ions).

7. **All heteropolymolybdate anions are decomposed by strongly basic solutions.** The final products are simple molybdate ions and either an oxyanion or a hydrous metal oxide of the hetero atom:



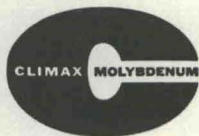
A limited number of heteropolymolybdates exist only in very acidic solutions. However, many exist in nearly neutral solutions, and some in neutral and even slightly basic solutions.

If hydroxyl ions are progressively added to a solution containing a given heteropolymolybdate, the pH generally rises steadily. The anion retains its identity throughout a range of pH until the pH of degradation for that anion is reached. Thereafter, the pH generally changes little as more hydroxyl ion is added until that species of heteropolymolybdate is either converted to another species stable in a higher pH range or completely degraded to simple ions.

8. **Throughout specific ranges of pH and other conditions, most solutions of heteropolymolybdates appear to contain predominantly one distinct species of anion.** It is generally reasonable to assume that this predominant species is identical with the anion existing in the solid state in equilibrium with the solution, or is closely related to it. Some heteropolymolybdates are remarkably stable, non-labile species.

TABLE I  
PRINCIPAL SPECIES OF HETEROPOLYMOLYBDATES

Number of atoms <i>X:Mo</i>	Principal hetero atoms	Typical formulas
1:12	Series A: P <sup>+5</sup> , As <sup>+5</sup> , Si <sup>+4</sup> , Ge <sup>+4</sup> , Sn <sup>+4</sup> (?), Ti <sup>+4</sup> , Zr <sup>+4</sup> Series B: Ce <sup>+4</sup> , Th <sup>+4</sup> , Sn <sup>+4</sup> (?)	$[\text{X}^{+n}\text{Mo}_{12}\text{O}_{40}]^{-(8-n)}$ $[\text{X}^{+n}\text{Mo}_{12}\text{O}_{42}]^{-(12-n)}$
1:11	P <sup>+5</sup> , As <sup>+5</sup> , Ge <sup>+4</sup>	$[\text{X}^{+n}\text{Mo}_{11}\text{O}_{39}]^{-(12-n)}$ (Possibly dimeric)
1:10	P <sup>+5</sup> , As <sup>+5</sup> , Pt <sup>+4</sup>	$[\text{X}^{+n}\text{Mo}_{10}\text{O}_{30}]^{-(22-60-n)}$ (Possibly dimeric)
1:9	Mn <sup>+4</sup> , Co <sup>+4</sup> , Ni <sup>+4</sup>	$[\text{X}^{+n}\text{Mo}_9\text{O}_{32}]^{-(10-n)}$
1:6	Te <sup>+6</sup> , I <sup>+7</sup>	$[\text{X}^{+n}\text{Mo}_6\text{O}_{24}]^{-(12-n)}$
2:18	P <sup>+5</sup> , As <sup>+5</sup>	$[\text{X}_2^{+n}\text{Mo}_{18}\text{O}_{62}]^{-(16-2n)}$
2:17	P <sup>+5</sup> , As <sup>+5</sup>	$[\text{X}_2^{+n}\text{Mo}_{17}\text{O}_{52}]^{-(22-102-2n)}$
2:12	Co <sup>+3</sup> , Al <sup>+3</sup> , Cr <sup>+3</sup> , Fe <sup>+3</sup> , Rh <sup>+3</sup>	$[\text{X}_2^{+n}\text{Mo}_{12}\text{O}_{42}]^{-(12-2n)}$
1 <i>m</i> :6 <i>m</i> ( <i>m</i> unknown)	Ni <sup>+2</sup> , Co <sup>+2</sup> , Mn <sup>+2</sup> , Cu <sup>+2</sup> , Se <sup>+4</sup> , P <sup>+3</sup> , As <sup>+3</sup> , P <sup>+5</sup>	$[\text{X}^{+n}\text{Mo}_6\text{O}_x]^{-(m(22-36-n))}$ <i>m</i>



## CLIMAX MOLYBDENUM COMPANY

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This bulletin, "Properties of Heteropolymolybdates", was prepared to help you evaluate this family of compounds which may be useful as:

- Solubilizers for heavy metals
- Precipitants for organic bases
- Oxidizing and reducing agents
- Humidifiers and dehumidifiers
- Catalysts for organic reactions

You may obtain laboratory-size samples of the following three heteropolymolybdates on request:

- (1) 12 series  $\text{Na}_4\text{SiMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$  Mol. wt > 1800
- (2) 12 series  $\text{Na}_3\text{PMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$  Mol. wt > 1800
- (3) 2:18 series  $\text{Na}_6\text{P}_2\text{Mo}_{18}\text{O}_{62} \cdot x\text{H}_2\text{O}$  Mol. wt > 2800

We would be pleased to discuss the applications of these and future heteropolymolybdates with you.

H. W. Schultze  
Climax Molybdenum Company  
Chemical Development Division

## USES

Certain heteropolymolybdates, notably the phosphomolybdates and phosphotungstomolybdates, are produced in large quantities by the color industry as precipitants for basic dyes, with which they form color lakes or toners.<sup>1</sup> Recent research has indicated that phospho- and silicomolybdates form the prosthetic groups of molybdenum-containing enzymes such as nitrate reductase.<sup>2</sup> In biological and analytical chemistry phosphomolybdates and silicomolybdates are widely used as reagents.<sup>3,4,5,6</sup> Other investigations have suggested that heteropolymolybdates may play an important role in such diverse phenomena as catalysis, and the resistance of stainless steel to corrosion.

## CLASSIFICATION

Heteropolymolybdates may be classified most conveniently by the ratio of the number of hetero atoms to molybdenum atoms. Compounds with the same numbers of atoms in the anion usually are isomorphous and have similar chemical properties. The best known heteropolymolybdate species are listed in Table I.

Besides these heteropolymolybdates a large number of other compounds exist where only the ratios of molybdenum atoms to hetero atoms are known. These may be divided somewhat arbitrarily into the two classes of Table II.

TABLE II  
OTHER SPECIES OF HETEROPOLYMOLYBDATES

Atomic ratio <i>X:Mo</i>	Principal hetero atoms
1: <6	P <sup>+3</sup> , As <sup>+3</sup> , Sb <sup>+3</sup> , P <sup>+5</sup> , As <sup>+5</sup> , S <sup>+4</sup> , Se <sup>+4</sup> , V <sup>+5</sup> , I <sup>+5</sup> , I <sup>+7</sup> , Co <sup>+3</sup> , Al <sup>+3</sup> (?), Fe <sup>+3</sup> (?), organic acids
1: >6 (but <12)	P <sup>+5</sup> , Mn <sup>+4</sup> (?), Mn <sup>+3</sup> (?), Ni <sup>+3</sup> (?)

## NOMENCLATURE

In this bulletin heteropolymolybdates are designated by prefixing the name of the hetero atom to the words "molybdate" or "molybdic acid"—for example, "phosphomolybdate" or "silicomolybdate." These are the ordinary names used by most chemists. Arabic numerals are used to describe the numbers of atoms of the hetero element and molybdenum. Roman numerals are used where necessary to designate lower valence states of the hetero atom.

However, the International Union of Pure and Applied Chemistry (IUC) uses a different system. Names of heteropolymolybdate anions begin with a number (Arabic numeral or Greek prefix) designating the *simplest ratio* of molybdenum atoms to hetero atoms. This is followed by the prefix "molybdo" and then by the name of the simple anion (or acid) which contains the hetero atom in the corresponding oxidation state. In case of ambiguity, Roman numerals may be used to designate the oxidation state of the hetero atom.

Examples of nomenclature by these two systems are shown in Table III.

TABLE III  
NOMENCLATURE OF HETEROPOLYMOLYBDATES

Formula	Names in this bulletin	IUC names
Na <sub>3</sub> [P <sup>+5</sup> Mo <sub>12</sub> O <sub>40</sub> ]	Sodium phospho-12-molybdate	Sodium 12-molybdophosphate Sodium dodecamolybdophosphate
H <sub>3</sub> [P <sup>+5</sup> Mo <sub>12</sub> O <sub>40</sub> ]	Phospho-12-molybdic acid	12-molybdophosphoric acid Dodecamolybdophosphoric acid
Na <sub>6</sub> [P <sub>2</sub> <sup>+5</sup> Mo <sub>18</sub> O <sub>62</sub> ]	Sodium 2-phospho-18-molybdate	Dimeric sodium 9-molybdophosphate
Na <sub>3</sub> [P <sub>2</sub> <sup>+3</sup> Mo <sub>12</sub> O <sub>41</sub> ]	Sodium 2-phosphorus(III)-12-molybdate	Sodium 6-molybdophosphite Sodium 6-molybdophosphorus(III) ate
Na <sub>3</sub> [Cr <sub>2</sub> <sup>+3</sup> Mo <sub>12</sub> O <sub>42</sub> ]	Sodium 2-chromi-12-molybdate	Dimeric sodium 6-molybdochromiate Dimeric sodium hexamolybdochromium(III) ate Dimeric sodium 6-molybdochromate(III)
Na <sub>8</sub> [Ce <sup>+4</sup> Mo <sub>12</sub> O <sub>42</sub> ]	Sodium ceri-12-molybdate	Sodium 12-molybdocerium(IV) ate Sodium dodecamolybdocerate
H <sub>8</sub> [Ce <sup>+4</sup> Mo <sub>12</sub> O <sub>42</sub> ]	Ceri-12-molybdic acid	12-molybdocerium(IV) acid Dodecamolybdocerium(IV) acid

## STRUCTURE

X-ray structural determinations have been made on compounds of the 1:12, 1:9, 1:6, 2:18, and 2:12 series and also on related isopolymolybdates and heteropolytungstates.

**REPRESENTATION** The simplest way to represent the anion structures is by polyhedra which share corners and edges with one another. Each Mo is at the center of an octahedron, and an O atom is located at each vertex of the octahedron. The Mo is small; each O is large (Figures 1, 2 and 3).

An  $\text{MoO}_6$  octahedron can share corners or edges (or both) with other  $\text{MoO}_6$  octahedra. When two octahedra share an edge, this means that two particular oxygen atoms form part of each octahedron (Figures 4 and 5).

The hetero atom (also small compared to an oxygen) is similarly located at the center of an  $\text{XO}_4$  tetrahedron or  $\text{XO}_6$  octahedron. Each such polyhedron containing the hetero atom is generally surrounded by  $\text{MoO}_6$  octahedra

which share corners or edges (or both) with it and with one another so that the correct total number of oxygen atoms is utilized. Each  $\text{MoO}_6$  octahedron is directly attached to a hetero atom through a shared oxygen atom. In the actual structures the octahedra are frequently slightly distorted.

Another common way of representing structures is by diagrams showing the locations of the centers of the various atoms. Figures 6a and 6b show the hetero-12-molybdate anion by this method and by the polyhedral method.

These methods of representation do not give pictures of the anions. They are merely diagrams which locate the positions of the centers of the atoms. They do not illustrate the fact that the oxygens are relatively large spheres, as shown in Figure 3. Therefore, they may give the misleading impression that there are large open spaces within the anions. In reality, practically all of the space within the anion structure is taken up by the bulky oxygens, which are either close-packed or nearly so.

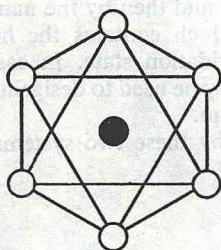


Figure 1

Locations of the centers of the atoms in an  $\text{MoO}_6$  octahedron. The black circle is Mo, the white circles O.

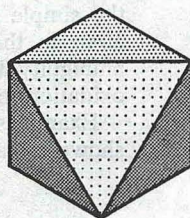


Figure 2

Diagram of an  $\text{MoO}_6$  octahedron to the same scale. Here the vertices represent the centers of the six O atoms.

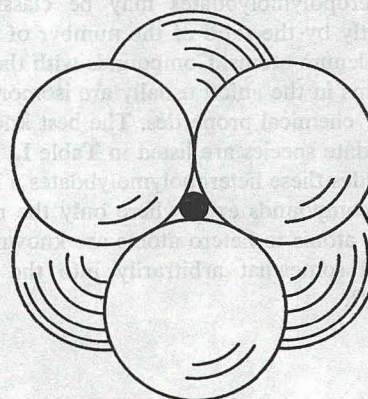


Figure 3

Diagram of an  $\text{MoO}_6$  octahedron to the same scale, but with the atoms shown full size. The Mo atom is the small black circle.

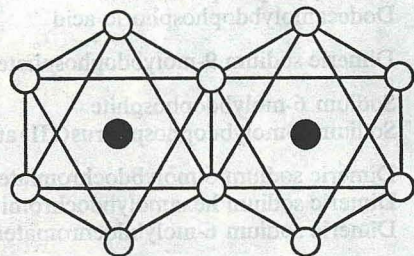


Figure 4

Two octahedra sharing an edge to form a structural unit  $\text{Mo}_2\text{O}_{10}$ . (This unit does not actually exist).

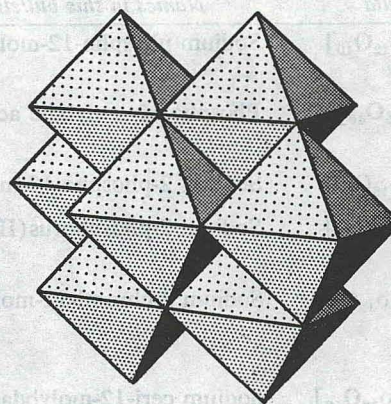


Figure 5

Structure of the paramolybdate ion  $[\text{Mo}_7\text{O}_{24}]^{-6}$ . Here seven  $\text{MoO}_6$  octahedra share edges to make the complete unit.<sup>40</sup>

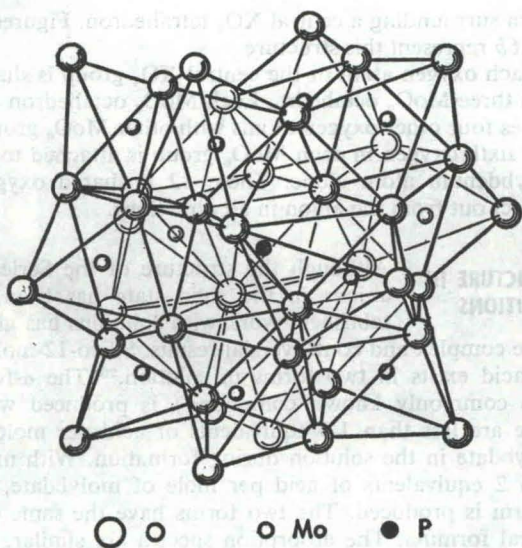


Figure 6a

Spatial diagram of the phospho-12-molybdate anion showing the locations of the centers of the various atoms, (Ref *d*).

### ROLE OF THE WATER OF HYDRATION

When the large heteropolymolybdate anions pack together as units in a crystal, the interstices between the anions are very large compared either to water molecules or to most simple cations. Molecules of water of hydration can fill up as much of this space as is not utilized by the cations. In most compounds there is apparently no direct linkage between the individual heteropolymolybdate anions. Instead, the complexes are joined by hydrogen bonding through some molecules of water of hydration.

Other water molecules are apparently often zeolytic—that is, they are lost on heating (or gained on cooling) continuously rather than stepwise at specific vapor pressures.<sup>7</sup> No great change of crystal structure accompanies the loss of this water. It has been suggested that the surfaces of heteropolymolybdate crystals which have been dehydrated by heating at moderate temperatures (150-300 C) should be very porous on a molecular scale and so have tremendous effective area.

However, in many cases there are non-zeolytic water molecules which cannot be lost continuously or without changing the arrangement of the complex anions.

These principles are illustrated in the crystal structure of phospho-12-tungstic acid hydrate, as determined by X-ray diffraction (Figure 7). The corresponding molybdenum compound exists.

Of the 29 water molecules, 17 are held together in a well-defined group by hydrogen bonding. The other 12 are not directly bonded to one another or to any of the first 17. These 12, plus the outer 6 from the first group of 17, are responsible for linking the anions together by hydrogen-bonding.

Heteropoly salts of larger cations, such as cesium, frequently crystallize as acid salts no matter what the ratio of cations to anions is in the mother liquor. Furthermore, salts of these cations are frequently less highly hydrated than salts of smaller cations. Apparently the larger cations

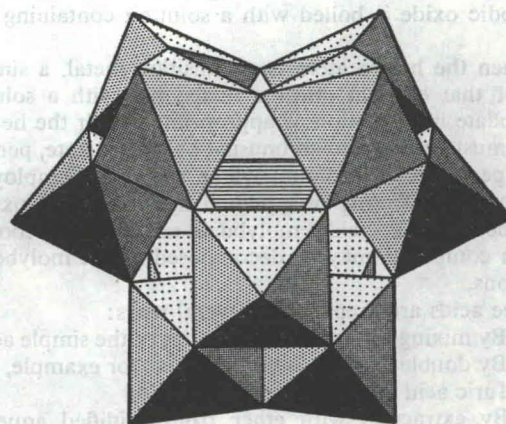


Figure 6b

Polyhedral diagram of the phospho-12-molybdate anion to the same scale as Figure 6a. Note the central tetrahedron.<sup>18</sup>

take up so much of the space between the heteropoly anions that there is less room left for water. In fact, there is often not enough room for all the large cations demanded by a normal salt formula. Instead, solvated hydrogen ions fill in to balance the negative charge of the anions and a crystalline acid salt results.

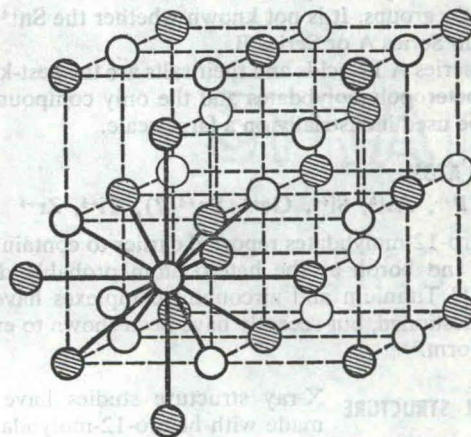


Figure 7

Structure of crystalline  $H_5[PW_{12}O_{40}] \cdot 29H_2O$ . Open circles represent centers of the  $[PW_{12}O_{40}]^{-4}$  units, and shaded circles the centers of the  $[H_5 \cdot 29H_2O]^{+4}$  units, (Ref *a*)

## PREPARATION

Heteropolymolybdates are always made in solution, generally after acidifying and heating theoretical quantities of reactants.

When the hetero atom is not a transition element, a soluble molybdate may be dissolved with a soluble salt containing the hetero atom in the appropriate oxidation state. The mixture is then acidified to an appropriate pH

range. Sometimes barium molybdate is mixed with a sulfuric acid solution containing the hetero atom, or molybdenic oxide is boiled with a solution containing the atom.

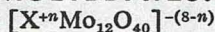
When the hetero atom is a transition metal, a simple salt of that element may be mixed hot with a soluble molybdate in a solution of appropriate pH. If the hetero atom must be raised to an unusual oxidation state, persulfate, peroxide or bromine water are often employed. Alternatively, freshly precipitated hydrous metal oxides may be boiled in acidic molybdate solutions, or coordination complexes may be decomposed in hot molybdate solutions.

Free acids are prepared in several ways:

1. By mixing appropriate quantities of the simple acids
2. By double decomposition of salts (for example, sulfuric acid plus a barium salt)
3. By extraction with ether from acidified aqueous solutions
4. By ion exchange from heteropolymolybdate salts

References (f), (g), (h), 3 and 9 contain valuable procedures.

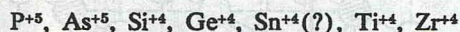
## HETERO-12-MOLYBDATES: SERIES A



Hetero-12-molybdates are apparently subdivided into two series.<sup>10</sup> The structure of Series A anions is built around a central  $XO_4$  tetrahedron. However,  $Ce^{+4}$  and  $Th^{+4}$  ions are too large to fit into the cavity at the center of a tetrahedron of oxygens. They do fit readily into the cavity at the center of an  $XO_6$  octahedron, and the Series B anions are probably constructed about central  $CeO_6$  and  $ThO_6$  groups. It is not known whether the  $Sn^{+4}$  complex is in Series A or Series B.

The series A 12-acids and their salts are the best-known of all heteropolymolybdates and the only compounds of this type used industrially on a large scale.

### HETERO ATOM



Hetero-12-molybdates reported earlier to contain manganese and boron as the hetero atom probably do not exist.<sup>11,12</sup> Titanium and zirconium complexes have also been questioned, but recently have been shown to exist in stable form.<sup>13</sup>

**CRYSTAL STRUCTURE** X-ray structure studies have been made with hetero-12-molybdates of  $P^{+5}$ ,  $As^{+5}$ ,  $Si^{+4}$ ,  $Ti^{+4}$ , and  $Zr^{+4}$ .<sup>13-18</sup> Similar studies have been made with the corresponding isomorphous 12-tungstates of  $B^{+3}$ ,  $Ge^{+4}$ ,  $P^{+5}$ ,  $As^{+5}$ , and  $Si^{+4}$ .<sup>19</sup> The anions all have the same symmetrical structure with 12  $MoO_6$  octa-

hedra surrounding a central  $XO_4$  tetrahedron. Figures 6a and 6b represent this structure.

Each oxygen atom of the central  $XO_4$  group is shared with three  $MoO_6$  octahedra. Each  $MoO_6$  octahedron also shares four other oxygen atoms with other  $MoO_6$  groups. The sixth oxygen in each  $MoO_6$  group is attached to the molybdenum atom alone. These 12 unshared oxygens project out from the anion in all directions.

### STRUCTURE IN SOLUTIONS

Although the structure of the Series A anions in the solid state has been established, work with solutions has given more complex and controversial results. Silico-12-molybdic acid exists in two forms in solution.<sup>20</sup> The  $\alpha$ -form (the commonly known compound) is produced when there are less than 1.5 equivalents of acid per mole of molybdate in the solution during formation. With more than 2 equivalents of acid per mole of molybdate, the  $\beta$ -form is produced. The two forms have the same empirical formula. The absorption spectra are similar, but the extinction coefficient of the  $\beta$ -form is about twice as great as that of the  $\alpha$ -modification. The  $\beta$ -form changes spontaneously and irreversibly to the  $\alpha$ -form over a period of several hours. It has been suggested that isomerisms of this kind result from a different arrangement of the 12  $MoO_6$  octahedra about the  $XO_4$  group.<sup>21</sup>

**MOLECULAR WEIGHT** All hetero-12-molybdates have molecular weights over 1800. The anion  $[SiMo_{12}O_{40}]^{-4}$  has an ionic weight of 1819.5.

**COLOR** All hetero-12-molybdate anions are yellow in solution and in most crystals. However, the  $Cr^{+3}$ ,  $Ni^{+2}$  and  $Cu^{+2}$  salts are green; the  $Co^{+2}$  salts are red or brown; and the  $Fe^{+3}$  salts may be reddish yellow. Precipitated salts of basic dyes usually retain the color of the original dye.

**BASICITY** Hetero-12-molybdic acids of Series A all have basicity  $(8-n)$  where  $n$  is the oxidation state of the hetero-atom. Higher basicities occasionally reported are probably in error because of degradation.

**HYDRATES** Most free hetero-12-molybdic acids of Series A form isomorphous 30-hydrates. These melt in their own water of hydration at 40-100 C. They begin to lose water in dry air and give up all 30 molecules over sulfuric acid. However, the constitutional water is held up to 375-425 C. Isomorphous lower hydrates also exist, which lose water without melting when heated.

Salts are nearly all highly hydrated, and numerous isomorphous series exist. Some examples are given in Table IV.

TABLE IV  
HYDRATES OF HETERO-12-MOLYBDATES

Hetero atom	Isomorphous hydrate series	Cation M
P	$M_3[PMo_{12}O_{40}]_2 \cdot 58H_2O$	Mg, Ca, Sr, Ba, Cd, Zn, Mn, Co, Ni
P	$M_3[PMo_{12}O_{40}]_2 \cdot 48H_2O$	Ca, Sr, Ba, Cd, Mn, Ni, Co
Si	$M_2[SiMo_{12}O_{40}] \cdot 31H_2O$	Cu, Mg, Zn, Mn, Ni, Co
Si	$M_2[SiMo_{12}O_{40}] \cdot 24H_2O$	Ca, Sr, Ba

Often dehydration and rehydration are reversible, as in the arseno-12-molybdates. Some hydrates of phospho-12-molybdic acid when heated at 300-350 C, are reported to form 2-phospho-18-molybdic acid.<sup>22</sup>

**SOLUBILITY** Free 12-acids are remarkably soluble in water (up to 85% by weight of solution) and in dilute acids, alcohols, and ether. Ether solutions appear to contain oxonium compounds. However, the free acids are insoluble in non-oxygenated solvents such as benzene, chloroform, and carbon disulfide.

Most metal salts are also highly soluble in water (up to 70% by weight of solution). However, rubidium, cesium, mercurous, and thallos salts are insoluble. Ammonium and potassium salts are often insoluble; this property is used in the determination of phosphorus by precipitation as  $(\text{NH}_4)_3 \text{PMo}_{12}\text{O}_{40} \cdot 2\text{HNO}_3 \cdot x\text{H}_2\text{O}$ .

Insoluble salts also form with many alkaloids, basic dyes, and other organic amines and amides.

Similar insoluble salts form with many cationic chelates of heavy metal atoms. Thus silico-12-molybdic acid precipitates Cu, Ag, Hg, Cd, Zn, Sn, Cr, Ni, and Co in the presence of ethylenediamine, thiourea, hexamethylenetetramine, dithiooxamide, or similar chelating agents.<sup>23</sup>

**EXTRACTION** Extraction of a free 12-acid from aqueous solution with ether results in formation of three layers. In order from top to bottom, the layers are:

1. Ether
2. Aqueous solution
3. Ether complex of the 12-acid

#### COMPLEXES WITH ORGANIC COMPOUNDS

Hetero-12-molybdates react with many organic oxy-compounds such as sugars, phenols, and acids to give products of unknown structure.<sup>3,20</sup>

**REDUCTION** The hetero-12-molybdates are strong oxidizing agents, comparable to chromic acid in oxidation potential.<sup>3,20</sup> Consequently they are readily reduced even by mild reducing agents. The reduced anions also have the atomic ratio 1X:12Mo. They are very dark blue, but otherwise show properties similar to those of the original anions. For example, the reduced phospho-12-molybdates form difficultly soluble ammonium salts, are precipitated by pyridine in acid solution, and may be extracted with ether. The reduced acids are readily reoxidized to their original states by bromine water, peroxide or other oxidants. However, they are not so readily reoxidized as phosphotungstates, which often reoxidize rapidly in air.

The sensitivity to reduction is apparently a direct consequence of the hetero-12-molybdate structure, since the hetero-11-molybdates (formed by degradation of the 12-anions) are insensitive to mild reducing agents. However, the 2-phospho-18-molybdates and the 2-arseno-18-molybdates are even more sensitive to reduction than the 12-anions.

In general, silicomolybdates and phosphomolybdates are more readily reduced than germanomolybdates. Furthermore, heteropolymolybdates are more readily reduced than corresponding heteropolytungstates. For example, in the phosphorus acids, the oxidizing power decreases in the order:

1. 2-phospho-18-molybdic acid (*strongest oxidant*)
2. Phospho-12-molybdic acid

3.  $\alpha$ -2-phospho-18-tungstic acid
4.  $\beta$ -2-phospho-18-tungstic acid
5. Phospho-12-tungstic acid (*weakest oxidant*)

Ferrous salts, sulfites, urea, uric acid, hydroquinone or other mild reducing agents are effective. Moderate reduction proceeds in definite steps corresponding to the addition of 2 or 4 electrons. However, strong reduction of the hetero-12-molybdates, for example with zinc and HCl, disintegrates the complexes completely. In such cases the reduced products have low molecular weights and give simple molybdates on reoxidation.

Moderate reduction of  $\alpha$ -silico-12-molybdic acid with  $\text{SnCl}_2$  gives two compounds: first, a green compound formed by addition of four electrons and, second, a blue complex formed by addition of one more electron on treatment with more  $\text{SnCl}_2$ . Both reduction products can be reoxidized with  $\text{HNO}_3$  in strongly acidic solution to give a quantitative yield of the original  $\alpha$ -acid. On reduction with  $\text{SnCl}_2$ , the  $\beta$ -acid gives only one product, a blue compound formed by addition of 4 electrons. The compound can be reoxidized, even by air, to the  $\beta$ -acid.<sup>20</sup> The atomic ratio in the reduced anions is 1X:12Mo.

Polarographic reductions of titano-12-molybdates and zircono-12-molybdates have been reported in detail.<sup>13</sup>

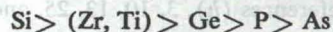
**OXIDATION** Ammonium hetero-12-molybdates (usually insoluble in water) dissolve in solutions of  $\text{H}_2\text{O}_2$ . The oxidized silicon complex is less soluble than the phosphorus one, and the two anions may be separated by using this difference. The structures and formulas of the oxidized products are unknown.

**DEGRADATION** Treatment with alkaline compounds degrades hetero-12-molybdates to products with fewer Mo atoms per hetero atom. The first degradation products appear to be hetero-11-molybdates and hetero-10-molybdates. Further treatment with bases leads to other stable species, mostly having ratios of one X to six or less Mo. In the phosphorus series, the 2-phospho-5-molybdate ion and salts are well established.<sup>26</sup> Finally, excess alkali causes complete degradation to simple molybdates. The overall degradation requires 20 to 28 moles of NaOH for each mole of 12-acid, the exact number depending upon the valence of the hetero atom and the chemistry of its simple acid.

Reference 26 contains a thorough description of degradation equilibria.

Another reaction similar to degradation is conversion of the phospho- and arseno-12-molybdates to 2-hetero-18-molybdates by treatment with bases. The conversion appears to proceed through the intermediate hetero-10-molybdates.

The different hetero-12-molybdates differ markedly in their stability to degradation. The order of stability is:



That is, the pH range of stability extends highest for the silicon complex, while very acidic solutions are required to keep the phospho-12-molybdate—and especially the arseno-12-molybdate—intact as 12-anions.

Thus silico-12-molybdic acid and the corresponding titanium and zirconium 12-acids may be neutralized intact by 4 KOH. Degradation begins only on further treatment with KOH—at about pH 4.5 for the Ti and Zr complexes and even then proceeds slowly. Few, if any, silicomolyb-



dates are known with less than 12 Mo atoms per Si atom, and no titanomolybdates or zirconomolybdates.

Germano-12-molybdic acid is also quite stable, although some degradation sets in before all four replaceable hydrogen ions have been neutralized. Germano-11-molybdic acid exists, but apparently there are no lower species.

With phospho-12-molybdic acid, hydrolytic degradation begins before neutralization of the three acidic hydrogens is complete. In very acidic solutions the anion is almost certainly intact as  $[\text{PMo}_{12}\text{O}_{40}]^{-3}$ . Recent determinations of molecular weight by ultracentrifugation suggest that the anion exists as a phospho-11-molybdate species at pH 4.5.<sup>24</sup> Isolation of the 11-salt  $\text{Na}_7[\text{PMo}_{11}\text{O}_{39}] \cdot x\text{H}_2\text{O}$  has been claimed. A number of 10-salts also appear to exist.

The arseno-12-molybdates are even less stable than the phospho-12-molybdates. The free acid has not been isolated, and the complex is very easily degraded. The only salts known are the slightly soluble  $\text{K}_3[\text{AsMo}_{12}\text{O}_{40}] \cdot 6\text{H}_2\text{O}$  and the difficulty soluble  $(\text{NH}_4)_3[\text{AsMo}_{12}\text{O}_{40}] \cdot 6\text{H}_2\text{O}$ . In solution most arsenopolymolybdates are readily converted to 2-arseno-18-molybdates. With arsenic these compounds are the most stable and best known heteropolymolybdates.

Besides this alkaline degradation, phospho-12-molybdates are also decomposed by excess of certain acids, such as phosphoric, iodic, periodic, hydrofluoric and concentrated hydrochloric and sulfuric. (However, nitric and dilute hydrochloric or sulfuric acids have no effect.) These acidic decompositions may convert the complexes to heteropolymolybdates with hetero atoms supplied by the added acid, or to molybdenyl compounds.

By comparison with heteropoly anions of other elements, molybdenum is of intermediate stability. With hetero-12-tungstates and hetero-12-vanadates, the stabilities follow the order:

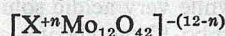


**PREPARATION** Hetero-12-molybdates are made by acidifying solutions of a molybdate, a salt of the hetero acid, and a salt of the metal cation. Special procedures are required in some cases. Strong acidification—generally to pH 1-2—is necessary to form the 12-anions. With insufficient acid 2-hetero-18-molybdate anions or lower compounds form. The free acids are obtained either by acidifying the salts with strong acids and extracting with ether or by hydrogen-cycle ion exchange.

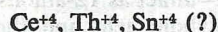
Because it is most resistant to degradation, the free silico-12-molybdic acid is easiest to prepare. The free phosphorus acid is fairly easily prepared if sufficient acid is used to prevent degradation. However, the free arseno-12-molybdic acid has not been made.

For detailed instructions on preparations of free acids and salts see references (h), 3, 10, 13, 25, and 26.

## HETERO-12-MOLYBDATES: SERIES B



### HETERO ATOM



**STRUCTURE** The structure of these compounds is probably similar to that of the hetero-12-molybdates of series A except that it is based on a central  $\text{XO}_6$

octahedron rather than an  $\text{XO}_4$  tetrahedron. These compounds are not isomorphous with those of Series A.

**COLOR** Compounds of this series are generally yellow.

**BASICITY** The basicity of the free acids is  $(12-n)$ , where  $n$  is the valence of the hetero atom. Since the known hetero atoms are all in the +4 state, the basicity of all known acids is eight.

**SOLUBILITY** The free acids and most salts are readily soluble. The normal ammonium and potassium salts are sparingly soluble in cold water, but dissolve in warm acidic solutions. The silver salts are insoluble.

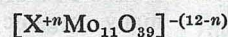
**ACID SALTS** With ceri-12-molybdic acid, the dissociation constants for the last two replaceable hydrogen ions are slightly smaller than the constants for the first six hydrogens. (The first six hydrogen ions all have dissociation constants of about  $10^{-2}$ ). A series of acid salts therefore exists with the formula  $\text{M}_6\text{H}_2[\text{XMo}_{12}\text{O}_{42}] \cdot x\text{H}_2\text{O}$ . A similar series of acid salts exists for the thorium complex.

**DEGRADATION** The cerium complex can be obtained undegraded in neutral solution. Appreciable degradation of the complex does not occur until the pH is raised to about 10.5.<sup>10</sup>

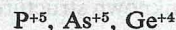
The tin complex is very susceptible to hydrolytic degradation. Little is known about it.

**PREPARATION** Hetero-12-molybdates of this series are prepared similarly to those of Series A.

## HETERO-11-MOLYBDATES



### HETERO ATOM



**STRUCTURE** These compounds are possible degradation products of hetero-12-molybdates. Their structure is unknown, but they may be dimeric and thus more suitably classed as 2-hetero-22-molybdates.

**PROPERTIES** Only the germano-11-molybdate anion is definitely known.<sup>11</sup> It exists in solution at pH above 4.8 in equilibrium with germanate, molybdate, and germano-12-molybdate anions. The upper limit of the pH range is not known.

Recent determinations of molecular weight by ultracentrifugation possibly indicate a monomeric phospho-11-molybdate as the principal species formed by dissolving phospho-12-molybdic acid in a buffer of pH 4.5.<sup>24</sup> Other evidence supports more strongly the existence of phospho-11-molybdates in solution.<sup>26</sup> Solid phospho-11-molybdates have also been reported. The 11-complexes appear to differ in properties from the 12-anions. For example, they are said to be relatively inert to reduction.

## HETERO-10-MOLYBDATES



### HETERO ATOM



**PROPERTIES** These compounds also appear to be degradation products of hetero-12-molybdates, but their existence is still controversial. The reported insoluble

silver and guanidinium salts of high basicity may not have been correctly formulated because of preparative and analytical difficulties.

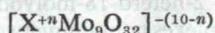
The structure of these anions may be dimeric and thus they may perhaps be more suitably classed as 2-hetero-20-molybdates.

Solutions and salts of these anions are reported to be yellow.

Extraction of phospho-10-molybdic acid with ether gives a system with three layers similar to that obtained with phospho-12-molybdates.<sup>27</sup> The ether complex layer always contains an atomic ratio P:Mo of 1:10, although the conditions and proportions in the other phases vary. The etherate thus appears to be a distinct compound of approximate composition  $H_3PO_4 \cdot 10MoO_3 \cdot 20Et_2O \cdot 64H_2O$ . Addition of NaCl to the aqueous phase inhibits formation of the ether complex. The same results are obtained when either HCl or  $HNO_3$  is added to vary the pH.

The existence of silico-10-molybdates is doubtful, although some enzyme systems involving heteropolymolybdates function most effectively when the atomic ratio Si:Mo is 1:10.<sup>2</sup>

## HETERO-9-MOLYBDATES



### HETERO ATOM

$Mn^{+4}, Ni^{+4}, Co^{+4} (?)$

### STRUCTURE

The hetero-9-molybdates are built around a central  $XO_6$  octahedron, as shown in Figure 8.<sup>28</sup> Piezoelectric studies and the X-ray determination show that the anion is asymmetric. Magnetic susceptibility studies confirm the oxidation states of the hetero atoms.

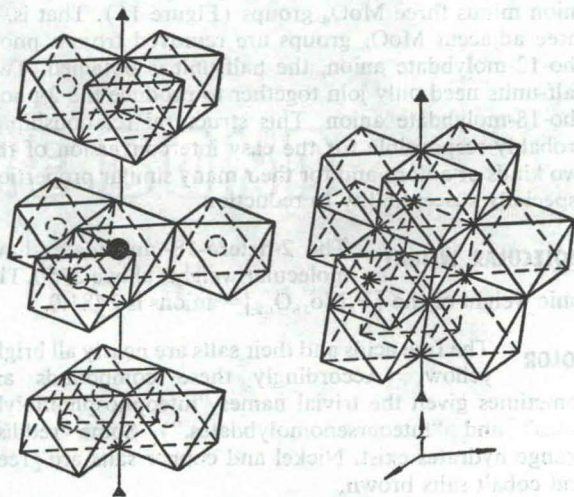


Figure 8

Structure of the asymmetric anion  $[MnMo_9O_{32}]^{6-}$ . Left, exploded view showing Mn atom (black circle) and Mo atoms (open circles). Right, view of complete ion.<sup>28</sup>

### MOLECULAR WEIGHT

Molecular weights of hetero-9-molybdates are over 1400. Ionic weight of the anion  $[MnMo_9O_{32}]^{6-}$  is 1430.5.

**COLOR** The mangan-9-molybdate anion is bright orange-red. The corresponding nickel anion is such a dark red that it is almost black. Its solutions are also very dark.

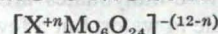
**BASICITY** This series has basicity  $(10-n)$  where  $n$  is the valence of the hetero atom. Since known hetero-atoms are all in the +4 state, in practice the basicity is always six.

**SOLUBILITY** The anions form isomorphous normal potassium and ammonium salts which are soluble in cold water.

**DEGRADATION** The hetero-9-molybdates and their colors are destroyed in solution by excess of bases or strong acids and by strong reducing agents.<sup>29</sup> The manganese and nickel complexes decompose in the pH range 6-7. However, the anions are stable to heat.

**PREPARATION** The hetero-9-molybdates are prepared by oxidizing a solution of a simple divalent salt of the hetero atom and a soluble paramolybdate  $M_6Mo_7O_{24}$  with persulfate, peroxide, bromine water, or permanganate.

## HETERO-6-MOLYBDATES



### HETERO ATOM

$Te^{+6}, I^{+7}$

Some compounds of unknown structure listed here with the 1*m*-hetero-6*m*-molybdates may also belong in this group.

**STRUCTURE** X-ray determinations on  $(NH_4)_6[TeMo_6O_{24}] \cdot 7H_2O$  and the isomorphous potassium salt show that the telluro-6-molybdate structure consists of seven octahedra all lying in one plane. The six  $MoO_6$  octahedra form a ring surrounding the central  $TeO_6$  octahedron. Each  $MoO_6$  shares one edge with each of its two neighboring  $MoO_6$  octahedra. Each  $MoO_6$  also shares an edge with the  $TeO_6$  octahedron (Figure 9).<sup>34</sup>

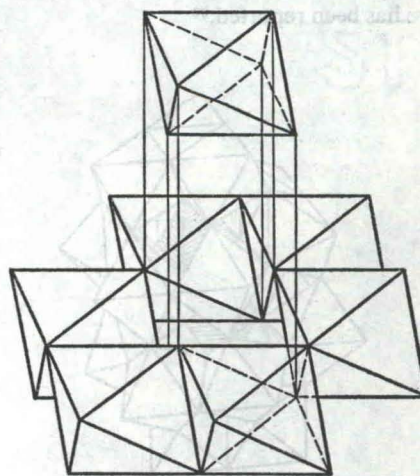


Figure 9

Structure of the ion  $[TeMo_6O_{24}]^{6-}$  with the central  $TeO_6$  octahedron elevated to show the annular arrangement of the six  $MoO_6$  octahedra, (Ref. b).

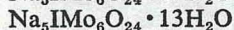
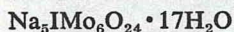
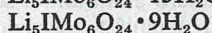
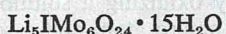
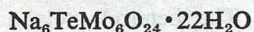
The structure of another telluromolybdate of empirical formula  $(\text{NH}_4)_2\text{O} \cdot 4\text{TeO}_3 \cdot 12\text{MoO}_3 \cdot 20\text{H}_2\text{O}$  has also been determined by X-ray diffraction. This compound is a double salt containing two discrete types of anions: (a) unattached  $\text{TeO}_6^{-3}$  anions and (b) telluro-6-molybdate anions of the structure above.

**MOLECULAR WEIGHT** The hetero-6-molybdates have molecular weights above 1050. The  $[\text{TeMo}_6\text{O}_{24}]^{-6}$  anion has an ionic weight of 1087.3.

**COLOR** Hetero-6-molybdates are white or yellowish.

**BASICITY** Basicity of these compounds is  $(12-n)$  where  $n$  is the valence of the hetero atom.

**HYDRATES** Salts of this series are heavily hydrated. Some typical hydrates are:



**SOLUBILITY** Hetero-6-molybdates are generally readily soluble in water, but a few heavy metal salts are insoluble.

**DEGRADATION** Hetero-6-molybdates are stable at pH values above the stability range for hetero-12-molybdates or 2-hetero-18-molybdates. However, in neutral or basic solution they are degraded to compounds of lower ratio or to simple salts.

**PREPARATION** Telluro-6-molybdates are prepared by acidifying solutions containing a tellurate and a molybdate or by adding a base to a mixture of telluric and molybdic acids.

Iodo-6-molybdates are prepared similarly. The free acid is made directly from periodic and molybdic acids. It may also be prepared by reaction between barium molybdate, periodic acid and sulfuric acid. Its neutralization curve has been reported.<sup>30</sup>

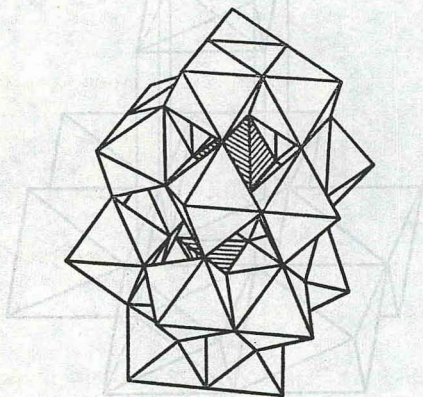


Figure 10

Structure of the dimeric anion  $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{-6}$ . The corresponding 2-hetero-18-molybdates have a similar structure.<sup>31</sup>

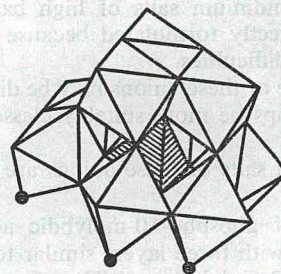
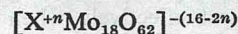


Figure 11

The half-unit obtained by splitting the 2-hetero-18-molybdate structure.<sup>31</sup> This half-unit may also be obtained by removing three  $\text{MoO}_6$  octahedra from the hetero-12-molybdate structure (Figure 6b).

## 2-HETERO-18-MOLYBDATES



### HETERO ATOM

$\text{P}^{+5}, \text{As}^{+5}$

**STRUCTURE** The 2-hetero-18-molybdates are dinuclear complexes containing two central  $\text{XO}_4$  tetrahedra surrounded by 18  $\text{MoO}_6$  octahedra. Although the structures of these particular compounds have not been determined by X-ray, the structure of the corresponding 2-phospho-18-tungstate anion has been worked out (Figure 10).<sup>31</sup> There is little doubt that the 2-hetero-18-molybdates have the same structure, especially since they have the identical dimeric formula and analogous properties and methods of preparation.

The half-unit obtained by splitting the dimer has exactly the same structure as the phospho-12-molybdate anion minus three  $\text{MoO}_6$  groups (Figure 11). That is, if three adjacent  $\text{MoO}_6$  groups are removed from a phospho-12-molybdate anion, the half-unit is obtained. Two half-units need only join together to produce the 2-phospho-18-molybdate anion. This structural relationship is probably responsible for the easy interconversion of the two kinds of anions and for their many similar properties, especially susceptibility to reduction.

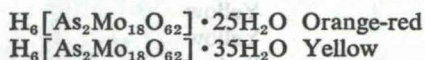
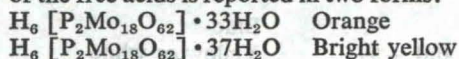
**MOLECULAR WEIGHT** The 2-hetero-18-molybdates have molecular weights above 2750. The ionic weight of the  $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{-6}$  anions is 2781.0.

**COLOR** The free acids and their salts are nearly all bright yellow. (Accordingly these compounds are sometimes given the trivial names "luteophosphomolybdates" and "luteoarsenomolybdates.") Some reddish orange hydrates exist. Nickel and copper salts are green and cobalt salts brown.

**BASICITY** The acids are 6-basic. Guanidinium, cesium, silver, and thallium salts of other basicities have sometimes been reported, but these are almost certainly mixtures.

**HYDRATION** The crystalline free acids and salts are all highly hydrated. Corresponding compounds of the phosphorus and arsenic series differ in their

amounts of water of crystallization. For example, each of the free acids is reported in two forms:



The higher hydrates of both acids are unstable at ordinary temperatures.

**SOLUBILITY** Free 2-hetero-18-molybdic acids are exceptionally soluble in water (up to 85% by weight of solution), ether, absolute alcohol, and cold nitric acid. (But the 2:18 arseno-acid is decomposed by hydrochloric and sulfuric acids.) However, they are insoluble in non-polar solvents such as chloroform, carbon disulfide, or hydrocarbons.

Ammonium salts of both acids are readily soluble. This property may be used to remove traces of phospho-12-molybdic acid from 2-phospho-18-molybdic acid. However, salts of pyridine, alkaloids, and some other organic bases are insoluble.

Most metal salts are readily soluble in water. However, the potassium salt of the 2:18 phosphorus acid is only slightly soluble in cold water. Rubidium and cesium salts are quite insoluble. This is the basis of an analytical separation of alkali metals.<sup>22</sup> In the arsenic series the lead, mercurous, silver, cesium, and thallos salts are insoluble.

**REDUCTION** As discussed under the 12-acids, the 2-hetero-18-molybdates are extremely readily reduced—more readily than the phospho-12-molybdates or any of the phosphotungstates. With mild reducing agents such as ferrous salts, sulfites, or uric acid, reduction proceeds in definite stages corresponding to the addition of 2, 4, or 6 electrons. The reduced anions are colored an intense blue, but show all the properties of their parent anions. They are soluble, but can be crystallized by adding common ions. They are oxidized by bromine water or peroxide to the original materials. The blue solutions obey Beer's Law, and hence can be used for colorimetric measurements.

The anions are also reduced when exposed to the surfaces of many free metals.

**DEGRADATION** The 2-phospho-18-molybdates are apparently degraded by small amounts of hydroxides or carbonates to 2-phospho-17-molybdates of the type  $\text{M}_{10}[\text{P}_2\text{Mo}_{17}\text{O}_{61}] \cdot x\text{H}_2\text{O}$ . Treatment with HCl regenerates the 2:18-acid. Addition of excess base leads to complete decomposition of the complex between pH 4.5 and 5.5.

Salts of the 2:18 arsenic series are more stable than the corresponding phosphorus compounds under most conditions. However, they are slowly converted to colorless salts of lower complexity on long standing with their mother liquors. Their range of complete degradation lies between pH 4 and 6.5. The 2:18 arsenates are also decomposed by excess sulfuric or hydrochloric acids.

**CONVERSION TO OTHER COMPLEXES** The 2-hetero-18-molybdates may represent metastable equilibrium states in some ranges of pH and concentration where they are well known.<sup>26</sup> Thus dilute free acids prepared by ion exchange contain the 2:18 complexes as virtually the sole anionic species. However, if

the temperature is raised above 35 C, other complexes may develop irreversibly. Still other complexes develop irreversibly on long standing. For example, upon standing in some solutions at room temperature, the 2-phospho-18-molybdate complex very gradually converts to the phospho-12-molybdate.

Solutions of heteropolymolybdates appear to contain trace amounts of many of the other possible species in equilibrium. The equilibria are complicated by rate phenomena. However, removal of any one heteropoly species, as by precipitation, eventually leads to complete conversion to that form. Thus ammonium 2-phospho-18-molybdate in solution will eventually precipitate out as the insoluble ammonium phospho-12-molybdate. Heating greatly accelerates this reaction.

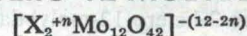
The 2-phospho-18-molybdates may also be converted to phospho-12-molybdates by treatment with acid. In turn, the reverse reaction may be brought about by treatment with base or additional phosphoric acid.

**DISSOCIATION CONSTANTS** The dissociation constants of 2-phospho-18-molybdic acid all lie in the range  $10^{-2}$  to  $10^{-3}$ . With the 2-arseno-18-molybdic acid the constants lie between  $10^{-2}$  and  $10^{-3.5}$ .

**PREPARATION** The 2-hetero-18-molybdates are prepared at higher temperatures, higher concentrations, and under slightly less acid conditions than the 12-anions.<sup>3,25</sup> The range of conditions necessary for formation is narrower than for other species. Once formed, however, the 2:18 anions remain undecomposed under conditions in which they would not form.

The free acids may be prepared by acidifying solutions of the salt, and extracting with ether.<sup>3</sup> Alternatively, they may be produced from salt solutions by passage through an ion-exchange column.<sup>8</sup> Salts of the arsenic complex may be prepared by simply saturating solutions of arsenates with  $\text{MoO}_3$ . The 2-phospho-18-molybdic acid has been prepared by controlled heating of the crystals of the 12-acid at 300-350 C followed by water extraction of the mass.<sup>22</sup>

## 2-HETERO-12-MOLYBDATES



**HETERO ATOM**  $\text{Al}^{+3}, \text{Cr}^{+3}, \text{Fe}^{+3}, \text{Co}^{+3}, \text{Rh}^{+3}$

**STRUCTURE** A combination of magnetic susceptibility studies, partial X-ray investigation, and chemical evidence has demonstrated that these anions have a dimeric structure (2:12) based on  $\text{XO}_6$  octahedra. A structure consistent with all the evidence has been suggested but not proved<sup>9,32</sup>.

**MOLECULAR WEIGHT** The 2-hetero-12-molybdates have molecular weights above 1900. The  $[\text{Cr}_2\text{Mo}_{12}\text{O}_{42}]^{-6}$  anion has an ionic weight of 1927.4.

**COLOR** Complexes of each hetero atom have a characteristic color in solids and solution, for example:

Al	Colorless
Cr	Dark pink
Fe	Colorless
Co	Green
Rh	Amber

**BASICITY** All known 2-hetero-12-molybdates have the basicity  $(12-2n)=6$ , since  $n$  is always 3.

**HYDRATES** These complexes are highly hydrated. Most of the hydrate water is given up around 100 C, but some is held up to around 200-250 C.<sup>9</sup>

Corresponding salts of these anions are isomorphous, for example, the  $(\text{NH}_4)_6[\text{X}_2\text{Mo}_{12}\text{O}_{42}] \cdot 20\text{H}_2\text{O}$  series or the normal potassium salts.

**SOLUBILITY** The free acids are insoluble in ether, although extremely soluble in water. Nearly all the salts are also very soluble in water, but insoluble in organic solvents. The anions precipitate alkaloids, organic amines, cesium, and cationic coordination complexes.

**REDUCTION** The complexes are insensitive to mild reduction, but are decomposed by violent reduction.

**DEGRADATION** The stability and degradation ranges of pH for 2-hetero-12-molybdates are:

Hetero-atom	Approximate stability range, pH	Approximate range of complete degradation, pH
Al	<5	5-6
Cr	<5.5	5.5-6.5
Fe	<4.5	4.5-5.5
Co	<5	5-6

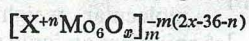
**THERMAL STABILITY** All these anions are very stable in solution and as solids, except that the iron and aluminum complexes decompose when heated in solution. However, the chromium and cobalt compounds are very stable in hot solution, and solutions of free acids may be kept unchanged for years. None of the complexes decomposes when the solid salts are heated at 250 C. All the salts can be completely dehydrated at lower temperatures without decomposing the anions.

**DISSOCIATION CONSTANTS** The dissociation constants for the six replaceable hydrogen ions of the free acids lie in the range  $10^{-1.5}$  to  $10^{-3.5}$ .

**PREPARATION** The 2-hetero-12-molybdates are prepared by mixing hot solutions of paramolybdates  $\text{M}_6[\text{Mo}_6\text{O}_{24}]$  and simple salts of the hetero atoms.<sup>9</sup> An oxidizing agent such as hydrogen peroxide must be added during the preparation of the cobaltic complex.

The free acids may be prepared from the salts by ion exchange and obtained as solids by evaporating their solutions. Upon evaporation of the pink acid of the chromic complex, a green solid acid separates, but this redissolves to form a pink solution.

### 1m-HETERO-6m-MOLYBDATES



#### HETERO ATOM

$\text{Cu}^{+2}$ ,  $\text{P}^{+3}$ ,  $\text{P}^{+5}$ ,  $\text{As}^{+3}$ ,  $\text{Se}^{+4}$ ,  $\text{Mn}^{+2}$ ,  $\text{Co}^{+2}$ ,  $\text{Ni}^{+2}$

**STRUCTURE** The structure, molecular weights, and degrees of polymerization  $m$  of these compounds are unknown. Some may be 2-hetero-12-molybdates—for example, the  $\text{P}^{+3}$  and  $\text{As}^{+3}$  complexes.

**COLOR** These compounds usually have colors characteristic of the hetero atom. Colors are:

Cu	Blue
P (+3 and +5)	Yellow or white
As	Yellow
Se	Yellow
Mn	Red
Co	Red
Ni	Blue

**STABILITY** The Mn complex is quite labile in solution. Stability of other complexes is not known.

**PREPARATION** The  $\text{P}^{+5}$  anions are prepared from molybdic acid and a metaphosphate or pyrophosphate.

### OTHER HETEROPOLYMOLYBDATES

A number of other heteropolymolybdates exist with various hetero atoms, as listed in Table II, page 3. Many complexes of unknown structure form by reaction between simple molybdates and various organic acids, especially dicarboxylic and hydroxy acids. Some of these acids are: phenols, formic, oxalic, lactic, malic, tartaric, citric, mucic, salicylic, protocatechualdehyde, gallic, pyrogalllic, catechol, hexahydrotetrahydroxybenzoic, and  $\alpha$ -hydroxynaphthoic.<sup>33</sup>

Some of these complexes have been characterized with greater certainty than others. Among these are:

Atomic ratios	Possible formulas
4M:2S <sup>+4</sup> :5Mo	$\text{M}_4[\text{X}_2^{+4}\text{Mo}_5\text{O}_{21}]$
4M:2Se <sup>+4</sup> :5Mo	
8M:3S <sup>+4</sup> :10Mo	$\text{M}_8[\text{X}_3^{+4}\text{Mo}_{10}\text{O}_{40}]$
8M:3Se <sup>+4</sup> :10Mo	
1M:1As <sup>+5</sup> :3Mo	$\text{M}[\text{As}^{+5}\text{Mo}_3\text{O}_{12}]$
2M:1P <sup>+5</sup> :2Mo	$\text{M}_2[\text{P}_2^{+5}\text{Mo}_4\text{O}_{19}]$
6M:2P <sup>+5</sup> :5Mo	$\text{M}_6[\text{P}_2^{+5}\text{Mo}_5\text{O}_{23}]$
2M:1P <sup>+3</sup> :6Mo	$\text{M}_2[\text{P}_2^{+3}\text{Mo}_{12}\text{O}_{44}]$
4M:2P <sup>+3</sup> :5Mo	$\text{M}_4[\text{P}_2^{+3}\text{Mo}_5\text{O}_{20}]$
1M:1I <sup>+5</sup> :1Mo	$\text{M}[\text{I}^{+5}\text{MoO}_6]$
3M:2V <sup>+5</sup> :6Mo	$\text{M}_3[\text{V}_4^{+5}\text{Mo}_{12}\text{O}_{49}]$
2M:1(oxalate):1Mo	$\text{M}_2[\text{C}_2\text{MoO}_7]$
2M:1(oxalate):2Mo	$\text{M}_2[\text{C}_2\text{Mo}_2\text{O}_{10}]$
2M:2(oxalate):1Mo	$\text{M}_2[\text{C}_4\text{MoO}_{10}]$
3M:1(oxalate):V <sup>+5</sup> :3Mo	$\text{M}_3[\text{C}_2\text{VMo}_3\text{O}_{16}]$

Several derivatives exist for each of these series. The 2P:5Mo series is particularly well characterized. Its salts are colorless. It is the next stable degradation product following the yellow 12-, 11-, and 10-complexes.<sup>26</sup>

A large number of other heteropolymolybdates have been reported, frequently single compounds not members of any series. In many cases the compounds are probably definite double salts or acid salts.

Of especial interest are the compounds formed by phosphoric esters (for example, of glycerine), and by aryl and alkyl arsenates.

## OTHER HETEROPOLY COMPLEXES

Tungsten, uranium, vanadium, niobium, tantalum, and other elements also form heteropoly acids and salts. The tungsten and vanadium complexes are best known.

Heteropolytungstates are generally similar to heteropolymolybdates. However, heteropolymolybdates and heteropolytungstates of the same atomic ratios do not always have similar structures or properties. In general, the hetero-12-molybdates are less stable to basic degradation than the corresponding hetero-12-tungstates; that is, they undergo degradation at lower pH. Also, the heteropolymolybdates are stronger oxidizing agents than the corresponding heteropolytungstates.

Although the heteropolyvanadates are an extremely numerous class of compounds, practically nothing is known about their structures or true formulas. The structures probably involve different fundamental polyhedral units such as  $VO_5$  triangular bipyramids and  $VO_4$  tetrahedra.<sup>34,35</sup> Many of the compounds are more labile than the heteropolymolybdates, and equilibria involving cationic vanadyl species may be common.

## MIXED HETEROPOLY COMPLEXES

Molybdenum and tungsten form mixed heteropoly anions in which some of the  $MoO_6$  octahedra surrounding the hetero atom have been replaced by  $WO_6$ . Definite compositions may be obtained, but the exact placement of the  $MoO_6$  and  $WO_6$  octahedra is not known.

The properties of these mixed compounds are usually intermediate between those of the corresponding heteropolymolybdates and heteropolytungstates. For example, the sensitivity to reduction of the mixed heteropolytungstomolybdates increases with molybdenum content. Thus colors formed by precipitation of basic dyes with phospho-12-molybdic acid (PMA) tend to darken and lose brilliance under exposure to light. The analogous phospho-12-tungstate (PTA) pigments fade. The mixed phosphotungstomolybdic acid (PTMA) gives pigments of stable intermediate properties.<sup>1</sup>

Various mixed heteropolyvanadomolybdates have been prepared with phosphorus, arsenic, silicon, and oxalate as the hetero group, but very little is known about their chemistry. For unmixed heteropoly anions no atomic ratios higher than 1X:12 W, Mo, or V are known; but mixed compounds of higher series have been reported, such as 1 Si:17(V+Mo).

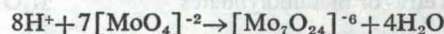
## ISOPOLYMOLYBDATES

When molybdate solutions are acidified in the absence of a hetero ion, the molybdates condense in definite steps to isopolymolybdates. Some isopolymolybdate structures in crystals have recently been determined by X-ray diffraction.

The molecular weights in solution have been studied by various methods. The results of light scattering measurements,<sup>36</sup> thermometric titrations,<sup>37</sup> spectrophotometric studies,<sup>38</sup> conductometric titrations,<sup>9,39,40</sup> and X-ray dif-

fraction studies<sup>40</sup> are all in agreement. However, earlier diffusion measurements have not been supported by this later work.<sup>41</sup>

In strongly basic solution molybdate ion exists as  $[MoO_4]^{-2}$ . As the solution is acidified, polymerization begins at about pH 6. The first step produces paramolybdate ion  $[Mo_7O_{24}]^{-6}$ :



No anionic species containing more than one, but less than seven, Mo atoms appears to exist in any appreciable proportion. As acidification proceeds, the next species formed is  $[Mo_8O_{26}]^{-4}$ . These two ions are formed and exist in the pH range 6–1.5.

The structure of the paramolybdate ion  $[Mo_7O_{24}]^{-6}$  in solids is shown in Figure 5, and the structure of  $[Mo_8O_{26}]^{-4}$  in Figure 12.

As a result of older systems of nomenclature, the octamolybdate ion  $[Mo_8O_{26}]^{-4}$  is commonly called a "tetramolybdate" or "metamolybdate." It is the anionic species present in solids of empirical formula  $M_2O \cdot 4MoO_3 \cdot xH_2O$ , better formulated as  $M_4[Mo_8O_{26}] \cdot xH_2O$ .

Further acidification, below pH 1.5, leads to more highly polymeric isopolymolybdates of unknown structures and formulas. A 10-molybdate or a 12-molybdate may exist at pH 1.

At pH 0.9, molybdic acid reaches its isoelectric point and gradually precipitates almost completely as hydrated molybdic oxide. At still lower pH, some molybdenum redissolves to form cationic species. These are presumably molybdenyl complexes such as  $MoO_2^{+2}$  or  $MoO^{+4}$ . However, in some cases the cations formed undoubtedly contain the anion of the added acid—for example, chloride.

Alkali metal and ammonium isopolymolybdates are soluble in water, sometimes more so than the corresponding simple molybdates. Isopolymolybdates of the lighter alkaline earth metals are also fairly soluble in water. Some heavy metal isopolymolybdates are also soluble.

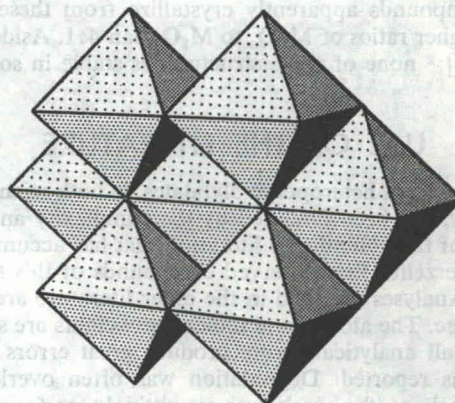


Figure 12

Structure of the "tetramolybdate" anion  $[Mo_8O_{26}]^{-4}$  in crystals.<sup>40</sup>

## SOLID ISOPOLYMOLYBDATES

Besides the paramolybdates  $M_6[Mo_7O_{24}] \cdot xH_2O$  and "tetramolybdates" or "metamolybdates"  $M_4[Mo_8O_{26}] \cdot xH_2O$ , several other kinds of iso-

TABLE V  
NAMES AND FORMULAS OF ISOPOLYMOLYBDATES

Name	Empirical formula	Correct formula
Normal or orthomolybdates	$M_2O \cdot MoO_3 \cdot xH_2O$	$M_2MO_4 \cdot xH_2O$
Tetra- or metamolybdates	$M_2O \cdot 4MoO_3 \cdot xH_2O$	$M_4[Mo_8O_{26}] \cdot xH_2O$
Paramolybdates	$3M_2O \cdot 7MoO_3 \cdot xH_2O^*$	$M_6[Mo_7O_{24}] \cdot xH_2O$
Octamolybdates	$M_2O \cdot 8MoO_3 \cdot xH_2O$	$M_2H_2[Mo_8O_{26}] \cdot xH_2O$
Trimolybdates	$M_2O \cdot 3MoO_3 \cdot xH_2O$	$M_{10}[Mo_7O_{24}][Mo_3O_{26}] \cdot xH_2O (?)$
Decamolybdates	$M_2O \cdot 10MoO_3 \cdot xH_2O$	(?)
Hexadecamolybdates	$M_2O \cdot 16MoO_3 \cdot xH_2O$	(?)

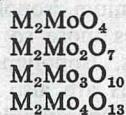
\*Often reported incorrectly as  $5M_2O \cdot 12MoO_3 \cdot xH_2O$ , since  $3/7 \approx 5/12$ .

polymolybdates exist in the solid phase. In the past these have been named on the basis of their empirical formulas.

Correct formulas are listed on Table V.

The octamolybdates lose water and decompose on heating. Decamolybdates apparently have a completely different structure. While other isopolymolybdates are white, the decamolybdates are yellow. They do not coagulate albumin as the tetra- and octamolybdates do. Finally, they are considerably less soluble than other isopolymolybdates.

In anhydrous melts, isopolymolybdates form four crystalline series:



These compounds frequently involve  $MoO_4$  tetrahedra in their structures, and sometimes  $MoO_6$  octahedra also. No compounds apparently crystallize from these melts with higher ratios of  $MoO_3$  to  $M_2O$  than 4:1. Aside from  $[MoO_4]^{-2}$  none of these structures is stable in solution.

## USE OF THE LITERATURE

Wider use of heteropolymolybdates, in both science and industry, has been hindered by the complexity and confusion of the voluminous literature that has accumulated since Berzelius first observed compounds of this type in 1826. Analyses reported in the older literature are often imprecise. The atomic and molecular weights are so high that small analytical errors produce great errors in the formulas reported. Degradation was often overlooked, and much of the work was unwittingly performed on mixtures. Accordingly the earlier literature, though often extremely valuable, should be used carefully and interpreted in the light of more recent findings.

Caution is especially necessary when:

1. Formulas are reported for salts of cations that usually precipitate many different species of molybdates, for example  $CN_3H_6^+$  (guanidinium),  $Hg_2^{+2}$ ,  $Ag^+$ ,  $Cs^+$ .

2. Analyses were obtained by difference (except in the case of  $H_2O$ ).
3. Preparations involved conditions that partially decompose heteropolymolybdates.
4. Commercial preparations were accepted as pure without further check.

**SYSTEMS OF FORMULATION** The literature on heteropolymolybdates uses four systems of writing formulas:

1. *Empirical or oxide formulas.* These express atomic ratios and oxidation states, but give no structural information. They are still used when structural information is lacking.
2. *Miolati-Rosenheim formulas.* The elaborate Miolati-Rosenheim theory, now outmoded, dominated the field of heteropoly compounds for several decades, and much of the literature is written in terms of it. In Miolati-Rosenheim formulas  $[MoO_4]^{-2}$  ions or the now discarded  $[Mo_2O_7]^{-2}$  ions are represented as coordinated to the hetero atoms. The Miolati-Rosenheim formulas are still frequently used deliberately to indicate that modern structural information is lacking.
3. *Variants of modern formulas.* Some authors indicate whether the hetero atom is enclosed in a tetrahedron  $XO_4$  or an octahedron  $XO_6$ . Thus  $[GeMo_{12}O_{40}]^{-4}$  is sometimes written  $[GeO_4Mo_{12}O_{36}]^{-4}$ . Other authors rearrange formulas in other ways to indicate structure — for example,  $[Ge(Mo_3O_{10})_4]^{-4}$  to show that four groups of three  $MoO_6$  octahedra each, surround the hetero atom in germano-12-molybdates.
4. *International Union of Pure and Applied Chemistry (IUC) formulas.* The official system of the IUC is little used. In this system silico-12-molybdic acid and its sodium salt are written  $H_4SiO_4 \cdot 12MoO_3 \cdot xH_2O$  and  $Na_4SiO_4 \cdot 12MoO_3 \cdot xH_2O$ .

Examples of the first three systems are given in Table VI.

TABLE VI  
SYSTEMS OF FORMULATION

Modern formula	Empirical formula	Miolati-Rosenheim formula
$\text{Na}_3[\text{PMo}_{12}\text{O}_{40}] \cdot 10\text{H}_2\text{O}$	$3 \text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 24\text{MoO}_3 \cdot 20\text{H}_2\text{O}$	$\text{Na}_3\text{H}_4[\text{P}(\text{Mo}_2\text{O}_7)_6] \cdot 8\text{H}_2\text{O}$
$\text{K}_6[\text{Cr}_2\text{Mo}_{12}\text{O}_{42}] \cdot 20\text{H}_2\text{O}$	$3 \text{K}_2\text{O} \cdot \text{Cr}_2\text{O}_3 \cdot 12\text{MoO}_3 \cdot 20\text{H}_2\text{O}$	$\text{K}_3\text{H}_6[\text{Cr}(\text{MoO}_4)_6] \cdot 7\text{H}_2\text{O}$
$\text{H}_6[\text{As}_2\text{Mo}_{18}\text{O}_{62}] \cdot 35\text{H}_2\text{O}$	$\text{As}_2\text{O}_5 \cdot 18\text{MoO}_3 \cdot 38\text{H}_2\text{O}$	$\text{H}_{12}[\text{As}_2\text{O}_2(\text{Mo}_2\text{O}_7)_9] \cdot 32\text{H}_2\text{O}$

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The best short discussions of heteropoly anions may be found in the following texts:

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- (c) P. C. L. Thorne and E. R. Roberts, "F. Ephraim's Inorganic Chemistry", Fifth Ed., Interscience Publishers, New York, 1948, p 512-521.
- (d) W. Hüchel, "Structural Chemistry of Inorganic Compounds", Vol I, Elsevier Publishing Co, New York and Amsterdam, 1950, p 179-213.

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