

# Topics in Current Chemistry

## 76

Editorial Board: M.J.S. Dewar  
K. Hafner E. Heilbronner S. Ito  
J.-M. Lehn K. Niedenzu C.W. Rees  
K. Schäfer G. Wittig  
Managing Editor: F.L. Boschke

G. A. Tsigdinos  
Heteropoly Compounds of  
Molybdenum and Tungsten

G. A. Tsigdinos  
Sulfur Compounds of  
Molybdenum and Tungsten

G. Moh  
High-Temperature Metal Sulfide  
Chemistry



**Aspects  
of Molybdenum and  
Related Chemistry**

Springer-Verlag Berlin Heidelberg New York

**76**

**Topics in Current Chemistry**

Fortschritte der Chemischen Forschung

---

**Aspects of Molybdenum  
and Related Chemistry**



**Springer-Verlag**

**Berlin Heidelberg New York 1978**

---

This series presents critical reviews of the present position and future trends in modern chemical research. It is addressed to all research and industrial chemists who wish to keep abreast of advances in their subject.

As a rule, contributions are specially commissioned. The editors and publishers will, however, always be pleased to receive suggestions and supplementary information. Papers are accepted for "Topics in Current Chemistry" in English.

ISBN 3-540-08986-1 Springer-Verlag Berlin Heidelberg New York

ISBN 0-387-08986-1 Springer-Verlag New York Heidelberg Berlin

Library of Congress Cataloging in Publication Data. Main entry under title: Aspects of molybdenum and related chemistry. (Topics in current chemistry ; 76) Bibliography: p. Includes index. CONTENTS: Tsigidinos, G. A. Heteropoly compounds of molybdenum and tungsten. – Tsigidinos, G. A. Inorganic sulfur compounds of molybdenum and tungsten – their preparation, structure, and properties. [etc.] I. Molybdenum compounds—Addresses, essays, lectures. I. Tsigidinos, George A., 1929- Heteropoly compounds of molybdenum and tungsten. 1978. II. Tsigidinos, George A., 1929- Inorganic sulfur compounds of molybdenum and tungsten. 1978. III. Moh, Günter, 1929- High temperature sulfide chemistry. 1978. IV. Series. QD1.F58 vol. 76 [QD181.M7] 540'.8s [546'.534'2] 78-13469

This work is subject to copyright. All rights are reserved, whether the whole or part of the material is concerned, specifically those of translation, reprinting, re-use of illustrations, broadcasting, reproduction by photocopying machine or similar means, and storage in data banks. Under § 54 of the German Copyright Law where copies are made for other than private use, a fee is payable to the publisher, the amount of the fee to be determined by agreement with the publisher.

© by Springer-Verlag Berlin Heidelberg 1978  
Printed in Germany

The use of registered names, trademarks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

Typesetting and printing: Schwetzinger Verlagsdruckerei GmbH, 6830 Schwetzingen. Bookbinding: Konrad Tritsch, Graphischer Betrieb, 8700 Würzburg  
2152/3140 – 543210

---

---

Editorial Board:

Prof. Dr. <i>Michael J. S. Dewar</i>	Department of Chemistry, The University of Texas Austin, TX 78712, USA
Prof. Dr. <i>Klaus Hafner</i>	Institut für Organische Chemie der TH Petersenstraße 15, D-6100 Darmstadt
Prof. Dr. <i>Edgar Heilbronner</i>	Physikalisch-Chemisches Institut der Universität Klingelbergstraße 80, CH-4000 Basel
Prof. Dr. <i>Shô Itô</i>	Department of Chemistry, Tohoku University, Sendai, Japan 980
Prof. Dr. <i>Jean-Marie Lehn</i>	Institut de Chimie, Université de Strasbourg, 1, rue Blaise Pascal, B. P. 296/R8, F-67008 Strasbourg-Cedex
Prof. Dr. <i>Kurt Niedenzu</i>	University of Kentucky, College of Arts and Sciences Department of Chemistry, Lexington, KY 40506, USA
Prof. Dr. <i>Charles W. Rees</i>	Hofmann Professor of Organic Chemistry Department of Chemistry, Imperial College of Science and Technology, South Kensington, London SW7 2AY, England
Prof. Dr. <i>Klaus Schäfer</i>	Institut für Physikalische Chemie der Universität Im Neuenheimer Feld 253, D-6900 Heidelberg 1
Prof. Dr. <i>Georg Wittig</i>	Institut für Organische Chemie der Universität Im Neuenheimer Feld 270, D-6900 Heidelberg 1

Managing Editor:

Dr. <i>Friedrich L. Boschke</i>	Springer-Verlag, Postfach 105 280, D-6900 Heidelberg 1
Springer-Verlag	Postfach 105 280 · D-6900 Heidelberg 1 Telephone (0 62 21) 4 87-1 · Telex 04-61 723  Heidelberger Platz 3 · D-1000 Berlin 33 Telephone (0 30) 82 2001 · Telex 01-833 19
Springer-Verlag New York Inc.	175, Fifth Avenue · New York, NY 10010 Telephone 4 77-82 00

---

## Contents

---

Heteropoly Compounds of Molybdenum and Tungsten	
George A. Tsigdinos	1
Inorganic Sulfur Compounds of Molybdenum and Tungsten – Their Preparation, Structure, and Properties	
George A. Tsigdinos	65
High-Temperature Metal Sulfide Chemistry	
Günter Moh	107
Author Index 26–76	153

---

# Heteropoly Compounds of Molybdenum and Tungsten

George A. Tsigdinos

Climax Molybdenum Company of Michigan, Research Laboratory, A Subsidiary of AMAX Inc.,  
Ann Arbor, Michigan 48105, U.S.A.

*In Memory of my Wife Shirley*

## Table of Contents

<b>Introduction</b> . . . . .	4
<b>Classification</b> . . . . .	5
<b>Nomenclature</b> . . . . .	5
<b>Use of the Literature</b> . . . . .	8
Systems of Formulation . . . . .	10
<b>Typical Properties</b> . . . . .	10
<b>Preparation</b> . . . . .	12
12-Heteropoly Anions . . . . .	13
9-Heteropoly Anions . . . . .	14
6-Heteropoly Anions . . . . .	14
12-Heteropoly Anions with Transition Metals as Central or Peripheral Atoms . . . . .	14
Other Heteropoly Anions . . . . .	15
<b>Structure in the Solid</b> . . . . .	15
Representation . . . . .	15
<b>Structure in Solution</b> . . . . .	18
<b>Role of Water of Hydration</b> . . . . .	19
<b>12-Heteropoly Anions: Series A</b> . . . . .	21
Crystal Structure . . . . .	22
Molecular Weight . . . . .	22
Color . . . . .	22
Solubility . . . . .	23



Density of Salts . . . . .	23
Hydrates . . . . .	23
Basicity and Acid Strength . . . . .	25
Thermal Stability . . . . .	27
Complexes with Organic Compounds . . . . .	29
Applications in Chemical Analysis . . . . .	29
Oxidation . . . . .	30
Degradation . . . . .	30
<b>12-Heteropolymolybdates: Series B . . . . .</b>	<b>32</b>
Preparation . . . . .	32
Color . . . . .	32
Basicity . . . . .	32
Solubility . . . . .	32
Acid Salts . . . . .	33
Degradation . . . . .	33
Structural Studies . . . . .	33
<b>11-Heteropoly Anions . . . . .</b>	<b>34</b>
Structure . . . . .	34
Properties . . . . .	34
<b>10-Heteropoly Anions . . . . .</b>	<b>34</b>
Properties . . . . .	34
<b>9-Heteropoly Anions . . . . .</b>	<b>35</b>
Structure . . . . .	35
Molecular Weight . . . . .	35
Color . . . . .	36
Basicity . . . . .	36
Solubility . . . . .	36
Degradation . . . . .	36
Preparation . . . . .	36
<b>6-Heteropoly Anions . . . . .</b>	<b>36</b>
Structure . . . . .	36
Molecular Weight . . . . .	37
Color . . . . .	37
Basicity . . . . .	37
Hydrates . . . . .	38
Solubility . . . . .	38
Degradation . . . . .	38
Preparation . . . . .	38
<b>6-Heteropoly Anions: Series B . . . . .</b>	<b>38</b>
Structure . . . . .	39
Molecular Weight . . . . .	39
Color . . . . .	39
Basicity . . . . .	39

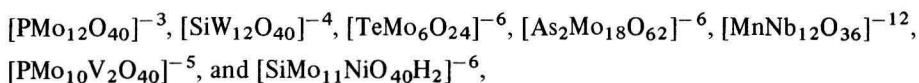
Hydrates . . . . .	39
Solubility . . . . .	40
Reduction . . . . .	40
Degradation . . . . .	40
Thermal Stability . . . . .	40
Preparation . . . . .	40
<b>1m-6m-Molybdates . . . . .</b>	<b>41</b>
Structure . . . . .	41
Color . . . . .	41
Stability . . . . .	41
Preparation . . . . .	41
<b>Dimeric 9-Heteropoly Anions . . . . .</b>	<b>41</b>
Structure . . . . .	42
Molecular Weight . . . . .	43
Color . . . . .	43
Basicity . . . . .	43
Hydration . . . . .	43
Solubility . . . . .	43
Degradation . . . . .	44
Conversion to Other Complexes . . . . .	45
Preparation . . . . .	45
<b>Oxidation-Reduction . . . . .</b>	<b>45</b>
Oxidation-Reduction Properties (General) . . . . .	46
Electrochemistry . . . . .	46
Heteropolymolybdate Blue Species . . . . .	49
<b>Other Heteropoly Compounds . . . . .</b>	<b>50</b>
Decamolybdodinicobaltate(III) Anion . . . . .	50
12-Heteropolytetraarsenate(V) Anion . . . . .	51
Tetramolybdo Complexes of Dialkyl and Diarylarsinates . . . . .	51
<b>Mixed Heteropoly Complexes . . . . .</b>	<b>53</b>
<b>Spectra of Heteropoly Compounds . . . . .</b>	<b>54</b>
Infrared . . . . .	54
Visible and Ultraviolet . . . . .	55
<b>Physical Measurements . . . . .</b>	<b>55</b>
<b>Uses . . . . .</b>	<b>56</b>
Catalysis . . . . .	56
Flame Retardants . . . . .	56
Corrosion Inhibition . . . . .	57
Miscellaneous . . . . .	57



## Introduction

The subject of heteropoly compounds has been covered in many recent reviews. This literature has primarily dealt with the structural chemistry and electronic properties of these complexes and has emphasized not only the heteropoly anions of molybdenum, but also those of tungsten and vanadium<sup>1-3</sup>. Equilibria in solution of heteropoly compounds have also been discussed<sup>4</sup>. In recent years, considerable interest has been shown in the heteropoly compounds of molybdenum not only in the structure and characterization of such compounds but also in those aspects of their chemistry that has made them of importance to industrial applications<sup>5</sup>. General aspects of the structure and properties of heteropoly compounds of molybdenum and tungsten have been presented in an earlier publication<sup>6</sup> and a critical evaluation of preparative procedures of heteropoly compounds has also appeared<sup>7</sup>. The present compilation constitutes an extensive updating of that earlier work<sup>6</sup> with the primary emphasis directed to the preparation, structure, properties, and uses of these compounds. Although only heteropoly compounds of molybdenum will be discussed in detail, some tungsten and other analogs will be included for comparison. No attempt has been made to summarize the complete literature in the field.

The heteropoly electrolytes constitute a large category of coordination-type salts and free acids with each member containing a complex and high-molecular weight anion. In these anions, two to eighteen hexavalent molybdenum (or tungsten) atoms surround one or more central atoms (heteroatoms). Vanadium, niobium, tantalum and transition metals can replace some of the molybdenum (or tungsten) atoms in the heteropoly structure. Typical examples are



where  $\text{P}^{+5}$ ,  $\text{Si}^{+4}$ ,  $\text{Te}^{+6}$ ,  $\text{As}^{+5}$ ,  $\text{Mn}^{+4}$ ,  $\text{P}^{+5}$  and  $\text{Si}^{+4}$  are the central atoms or heteroatoms, respectively. Over forty different elements can function as central atoms in distinct heteropoly anions, many of these in more than one series of these anions as will be discussed later.

In 1826 Berzelius first prepared and analyzed the heteropoly compound ammonium 12-molybdophosphate<sup>8</sup>. In 1854 Struve described the heteropoly molybdates of  $\text{Cr}^{+3}$  and  $\text{Fe}^{+3}$  but postulated these as double salts<sup>9</sup>. Marignac prepared 12-tungstosilicic acid in 1862 and recognized such compounds as a distinct class rather than double salts<sup>10</sup>. In 1908 Miolati made the first systematic attempt to understand the nature of heteropoly compounds by suggesting a structure for these compounds based on the ionic theory and Werner's coordination theory; Miolati's theory was extensively developed and applied by Rosenheim and his co-workers<sup>11</sup>. Although at present the nature of heteropoly compounds is well understood, these early theories served well as the groundwork for the future.

## Classification

Heteropoly compounds may be classified according to the ratio of the number of central atoms to the peripheral molybdenum or other such atoms. Compounds with the same number of atoms in the anion usually are isomorphous and have similar chemical properties. Usually, the heteropolymolybdates and heteropolytungstates containing nontransition elements as central atoms have more structural analogues than those that contain transition elements as central atoms. Table 1 lists all elements

Table 1. Elements capable of acting as central atoms (heteroatoms) in heteropoly compounds

Periodic Group	Element <sup>1)</sup>
I	H, Cu <sup>+2</sup>
II	Be <sup>+2</sup> , Zn <sup>+2</sup>
III	B <sup>+3</sup> , Al <sup>+3</sup> , Ga <sup>+3</sup>
IV	Si <sup>+4</sup> , Ge <sup>+4</sup> , Sn <sup>+4</sup> (?), Ti <sup>+4</sup> , Zr <sup>+4</sup> , Th <sup>+4</sup> , Hf <sup>+4</sup> , Ce <sup>+3</sup> , Ce <sup>+4</sup> , and other rare earths
V	N <sup>+5</sup> (?), P <sup>+3</sup> , P <sup>+5</sup> , As <sup>+3</sup> , As <sup>+5</sup> , V <sup>+4</sup> (?), V <sup>+5</sup> , Sb <sup>+3</sup> (?), Sb <sup>+5</sup> (?), Bi <sup>+3</sup>
VI	Cr <sup>+3</sup> , S <sup>+4</sup> , Te <sup>+4</sup> , Te <sup>+6</sup>
VII	Mn <sup>+2</sup> , Mn <sup>+4</sup> , I <sup>+7</sup>
VIII	Fe <sup>+3</sup> , Co <sup>+2</sup> , Co <sup>+3</sup> , Ni <sup>+2</sup> , Ni <sup>+4</sup> , Rh <sup>+3</sup> , Pt <sup>+4</sup> (?)

<sup>1)</sup> Some of these elements form heteropoly compounds only with molybdenum or only with tungsten. A question mark after the element denotes doubtful existence of a heteropoly anion.

known to be capable of acting as central atoms in heteropoly compounds. In several cases, the heteropoly compounds reported in the literature have not been characterized. The strychnine salt of the anion  $[N^{+5}Mo_{12}O_{40}]^{-3}$  has also been reported<sup>12)</sup> but its existence needs further verification.

Tables 2 and 3 illustrate the principal series of heteropolymolybdates and heteropolytungstates, respectively, which have been reported. Table 4 represents central atoms that form heteropoly anions, the composition and structure of which have not yet been elucidated.

## Nomenclature

The nomenclature of heteropoly compounds that has appeared in the literature has been inconsistent. Older designations consisted by prefixing the name of the central atom to the words "molybdate (tungstate)" or "molybdic (tungstic)" acid – for example, "phosphomolybdate" or "silicomolybdate". In addition, Greek prefixes were used to describe the numbers of atoms of the central element and molybdenum or tungsten, *i.e.*, dodecatungstosilicic acid. However, the International Union of Pure and Applied Chemistry (IUPAC) uses a different system<sup>13)</sup>. Names of heteropoly

6 Table 2. Principal series of heteropolymolybdates

Number of atoms X:W	Principal central atoms	Typical formulas	Central group	Structure by X-ray	Structure shown in Figure	Ref.
1:12	Series A: $N^{+5}(?)$ , $P^{+5}$ , $As^{+5}$ , $Si^{+4}$ , $Ge^{+4}$ , $Sn^{+4}(?)$ , $Ti^{+4}$ , $Zr^{+4}$ Series B: $Ce^{+4}$ , $Th^{+4}$ , $U^{+4}$	$[X^{+n}Mo_{12}O_{40}]^{-(8-n)}$	$XO_4$	Known	6, 8, 9	1, 81, 82, 95, 266, 267)
1:11	$P^{+5}$ , $As^{+5}$ , $Ge^{+4}$	$[X^{+n}Mo_{12}O_{42}]^{-(12-n)}$	$XO_{12}$	Known	14	92)
1:10	$P^{+5}$ , $As^{+5}$ , $Pt^{+4}(?)$	$[X^{+n}Mo_{11}O_{39}]^{-(12-n)}$	—	Unknown	—	—
1:9	$Mn^{+4}$ , $Ni^{+4}$	$[X^{+n}Mo_{10}O_x]^{-(2x-60-n)}$	—	Unknown	—	—
1:9	$P^{+5}$	$[X^{+n}Mo_9O_{32}]^{-(10-n)}$	$XO_6$	Known	15	138)
1:6	Series A: $Te^{+6}$ , $I^{+7}$ Series B: $Co^{+3}$ , $Al^{+3}$ , $Cr^{+3}$ , $Fe^{+3}$ , $Rh^{+3}$ , $Ga^{+3}$ , $Ni^{+2}$	$[X^{+n}Mo_9O_{31}(OH)_3]^{-(11-n)}$ $[X^{+n}Mo_6O_{24}]^{-(12-n)}$ $[X^{+n}Mo_6O_{24}H_6]^{-(6-n)}$	$XO_4$ $XO_6$ $XO_6$	Known Known Known	— — 7, 16	41) 144, 268, 269) 266, 78, 58)
2:10	$Co^{+3}$	$[X_2^{+n}Mo_{10}O_{38}H_4]^{-(12-2n)}$	$XO_6$	Known	23	181)
2:17	$P^{+5}$ , $As^{+5}$	$[X_2^{+n}Mo_{17}O_x]^{-(2x-102-2n)}$	—	Unknown	—	—
2:5	$P^{+5}$	$[X_2^{+n}Mo_5O_{23}]^{-(16-2n)}$	$XO_4$	Known	—	48, 49)
1m:6m (m unknown)	$Co^{+2}$ , $Mn^{+2}$ , $Cu^{+2}$ , $Se^{+4}$ , $P^{+3}$ , $As^{+3}$ , $P^{+5}$	$[X^{+n}Mo_6O_x]^{-(m(2x-36-n))}$	—	Unknown	—	—
4:12	$As^{+5}$	$[H_4As_4Mo_{12}O_{50}]^{-4}$	Cavity	Known	24	183)
1:1	$As^{+3}$	$[(CH_3)_2AsMoO_{14}OH]^{-2}$	$AsO_4$	Known	25	184)

Table 3. Principal series of heteropolytungstates

Number of atoms X:W	Principal central atoms	Typical formulas	Central group	Structure by X-Ray	Structure shown in Fig.	Ref.
1:12	$P^{+5}, As^{+5}, Si^{+4}, Ge^{+4}, Ti^{+4},$ $Co^{+2}, Cu^{+3}, Zn^{+2}, Cu^{+1}, Cu^{+2},$ $Ga^{+3}(?)$	$[X^{+n}W_{12}O_{40}]^{-(8-n)}$	$XO_4$	Known	6, 8, 9	1, 81, 82, 95, 266, 267)
1:10	$Si^{+4}, Pt^{+4}$	$[X^{+n}W_{10}O_x]^{-(2x-60-n)}$	$XO_4$	Unknown	—	—
1:9	$Be^{+2}$	$[X^{+2}W_9O_{31}]^{-6}$	—	Unknown	—	—
1:6	Series A: $Te^{+6}, I^{+7}$  Series B: $Ni^{+2}, Ga^{+3}$	$[X^{+n}W_6O_{24}]^{-(12-n)}$	$XO_6$	Isomorphous with 6-molyb- dates	7, 16	144, 268, 269)
		$[X^{+n}W_6O_{24}H_6]^{-(6-n)}$	$XO_6$	Isomorphous with 6-molyb- dates		58, 78, 266)
2:18	$P^{+5}, As^{+5}$	$[X_2^{+n}W_{18}O_{62}]^{-(16-2n)}$	$XO_4$	Known	17, 18	74)
2:17	$P^{+5}, As^{+5}$	$[X_2^{+n}W_{17}O_x]^{-(2x-102-2n)}$	—	Unknown	—	—
2:4:18	$X = P^{+5}, As^{+5}$ $Z = Mn^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2},$ $Zn^{+2}$	$[X_2^{+n}Z_4^{+m}W_{18}O_{70}H_4]^{-(28-2n+m)}$	$XO_4$	Known	Ref. 271)	1)
1m:6m (m unknown)	$As^{+3}, P^{+3}$	$[X^{+n}W_6O_x]_m^{-(2x-36-n)}$	—	Unknown	—	—

Table 4. Other species of heteropoly anions<sup>1)</sup>

Atomic ratio X:Mo	Atomic ratio X:W	Principal central 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> , Co <sup>+3</sup>
1:>6 (but <12)	—	P <sup>+5</sup> , Mn <sup>+4</sup> (?)
—	1:<6	P <sup>+3</sup> , As <sup>+3</sup> , Sb <sup>+3</sup> (?), Al <sup>+3</sup> , V <sup>+5</sup> , Mn <sup>+4</sup> , Bi <sup>+3</sup>
—	1:>6 (but <12)	Si <sup>+4</sup> (?), Zr <sup>+4</sup> , Ti <sup>+4</sup> , V <sup>+5</sup> , Sn <sup>+4</sup> (?), Pt <sup>+4</sup> (?)

<sup>1)</sup> Many of these species have not been characterized. It is possible that several of these are not true compounds.

anions begin with an Arabic numeral designating the simplest ratio of molybdenum or tungsten atoms to the central atom. This is followed by the prefix "molybdo" or "tungsto" and then by the name of the simple anion (or acid) which contains the central atom in the corresponding oxidation state. In case of ambiguity, Roman numerals may be used to designate the oxidation state of the central atom.

Current knowledge of the structure and properties of heteropoly compounds necessitates a more adequate nomenclature of such compounds by taking into consideration both the structure and degree of polymerization and oxidation of the central atom.

The proposed system of nomenclature is designed to extend the current IUPAC names to describe heteropoly compounds more adequately in cases where information about structure is currently available. In this system, the oxidation state of the central atom is shown by a Roman numeral in parentheses. The prefix molybdo, tungsto, or vanado designates the peripheral atoms, whereas the italicized prefix oct, tet, etc., indicates the stereochemistry (octahedral and tetrahedral) about the peripheral and central atoms. Arabic numerals designate the ratio of the number of peripheral and central atoms. The term dimeric, for example, preceding the name indicates the degree of polymerization of the heteropoly anion, when known. A superscript Arabic numeral at the end of the name indicates the charge of the anion. The Greek letter designates bridging between central atoms.

Examples of nomenclature of the IUPAC and the proposed systems are given in Table 5.

## 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 inaccurate since 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)

Table 5. Nomenclature of heteropoly compounds

Formula	Tentative IUPAC Names <sup>13</sup>	Proposed Names
$\text{Na}_3[\text{P}^{+5}\text{Mo}_{12}\text{O}_{40}]$	Trisodium dodecamolybdophosphate(V)	Sodium 12-oct-molybdo-tet-phosphate(V) <sup>3)</sup>
$(\text{NH}_4)_6[\text{P}_2^{+5}\text{Mo}_{18}\text{O}_{62}]$	Hexammonium 18-molybdodiphosphate(V)	Dimeric ammonium 9-oct-molybdo-tet-phosphate(V) <sup>6)</sup>
$\text{Na}_4[\text{NiW}_6\text{O}_{24}\text{H}_6]$	Tetrasodium hexawolframonicelate(II)	Sodium 6-oct-tungsto-oct-nickelate(II) <sup>4)</sup>
$(\text{NH}_4)_6[\text{Co}_2^{+3}\text{Mo}_{10}\text{O}_{38}\text{H}_4]$	Hexammonium 10-molybdodicobaltate(III)	Dimeric ammonium 5-oct-molybdo- $\mu$ -oct-dicobaltate(III) <sup>6)</sup>
$\text{Cs}_3\text{H}[\text{SiW}_{12}\text{O}_{40}]$	Tricesium monohydrogen dodecawolframolsilicate	Cesium molyhydrogen 12-oct-tungsto-tet-silicate(IV) <sup>4)</sup>
$\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$	12-Wolframasilicic acid	12-Oct-tungsto-tet-silicic(IV) <sup>4)</sup> acid
$\text{Na}_8[\text{Ce}^{+4}\text{Mo}_{12}\text{O}_{42}]$	Octasodium 12-molybdocerate(IV)	Sodium 12-oct-molybdocerate(IV) <sup>8)</sup>
$\text{K}_5[\text{P}^{+5}\text{Mo}_{10}\text{V}_2\text{O}_{40}]$	Pentapotassium decamolybdodivanadophosphate	10-Oct-molybdo-2-oct-vanado-tet-phosphate(V) <sup>5)</sup>

should be used carefully and interpreted in the light of more recent findings. Unfortunately, this trend continues to persist (though to a much smaller extent) in modern literature.

Caution is especially necessary when:

1. Formulas are reported for salts of cations that usually precipitate many different species of molybdates, *e.g.*,  $\text{CN}_3\text{H}_6^+$  (guanidinium),  $\text{Hg}_2^{+2}$ ,  $\text{Ag}^+$ ,  $\text{Cs}^+$ .
2. Analyses were obtained by difference (except in the case of water).
3. Preparations involved conditions that partially decompose heteropoly molybdates. In cases where impure materials were obtained because the precipitation methods used often coprecipitated impurities along with undecomposed heteropoly anion. For example, it was ascertained that addition of silver nitrate to a solution of 12-molybdophosphoric acid yields the desired salt partly decomposed, *i.e.*, the Ag to P ratio was 2.84/1.00 and that of Mo to P 11.18/1.00 rather than 3/1 and 12/1, respectively<sup>5)</sup>. Similarly, addition of four moles of silver nitrate to one mole of sodium 12-molybdosilicate yields only white insolubles whereas the same addition to 12-molybdosilicic acid has produced the pure salt, the effect here being one of pH<sup>5)</sup>. The preparation of free 12-molybdoarsenic acid from water dioxane solutions of sodium molybdate and arsenic acid has been described in the literature<sup>14)</sup> involving the addition of perchloric acid, but it was found<sup>15)</sup> that such procedures lead to high contamination by sodium and by perchlorate ions. The reported preparation of beta-12-molybdosilicic acid from water-ethanol mixtures<sup>16, 17)</sup> could not be reproduced without considerable contamination of the product with sodium perchlorate<sup>15, 18)</sup>. Caution should also be exercised in the preparation of heteropoly compounds by ion exchange techniques as several of these are degraded by the resins.
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 expressed with these formulas. In Miolati-Rosenheim formulas  $[\text{MoO}_4]^{-2}$  ions or the now discarded  $[\text{Mo}_2\text{O}_7]^{-2}$  ions are represented as coordinated to the central 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 central atom is enclosed in a tetrahedron  $\text{XO}_4$  or an octahedron  $\text{XO}_6$ ; thus  $[\text{GeMo}_{12}\text{O}_{40}]^{-4}$  is sometimes written  $[\text{GeO}_4\text{Mo}_{12}\text{O}_{36}]^{-4}$ . Other authors rearrange formulas in different ways to indicate structure; for example,  $[\text{Ge}(\text{Mo}_3\text{O}_{10})_4]^{-4}$ , shows that four groups of three  $\text{MoO}_6$  octahedra each surround the central atom in 12-molybdogermanates.

4. International Union of Pure and Applied Chemistry (IUPAC) formulas. The official system of the IUPAC is little used. In this system, 12-molybdosilicic acid and its sodium salt are written  $\text{H}_4\text{SiO}_4 \cdot 12 \text{ MoO}_3 \cdot x\text{H}_2\text{O}$  and  $\text{Na}_4\text{SiO}_4 \cdot 12 \text{ MoO}_3 \cdot x\text{H}_2\text{O}$ . Examples of the first three systems are given in Table 6.

Table 6. Systems of formulation

Modern formula	Empirical formula	Miolati-Rosenheim formula
$\text{Na}_3[\text{PMo}_{12}\text{O}_{40}] \cdot 10 \text{ H}_2\text{O}$	$3 \text{ Na}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 24 \text{ MoO}_3 \cdot 20 \text{ H}_2\text{O}$	$\text{Na}_3\text{H}_4[\text{P}(\text{Mo}_2\text{O}_7)_6] \cdot 8 \text{ H}_2\text{O}$
$\text{K}_4[\text{NiW}_6\text{O}_{24}\text{H}_6] \cdot 9 \text{ H}_2\text{O}$	$2 \text{ K}_2\text{O} \cdot \text{NiO} \cdot 6 \text{ WO}_3 \cdot 12 \text{ H}_2\text{O}$	$\text{K}_4\text{H}_6[\text{Ni}(\text{WO}_4)_6] \cdot 9 \text{ H}_2\text{O}$
$\text{H}_6[\text{As}_2\text{Mo}_{18}\text{O}_{62}] \cdot 35 \text{ H}_2\text{O}$	$\text{As}_2\text{O}_5 \cdot 18 \text{ MoO}_3 \cdot 38 \text{ H}_2\text{O}$	$\text{H}_{12}[\text{As}_2\text{O}_2(\text{Mo}_2\text{O}_7)_9] \cdot 32 \text{ H}_2\text{O}$

## Typical Properties

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

1. Heteropolymolybdates generally have very high molecular weights for inorganic electrolytes, ranging to over 4000.

2. Free acids and most salts of heteropoly anions are extraordinarily soluble in water and are often very soluble in several organic solvents as well.

In water: Most free acids are generally extremely soluble (up to 85% by weight of solution). In general, the heteropoly 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 heteropoly anion.  $\text{Cs}^+$ ,  $\text{Ag}^+$ ,  $\text{Tl}^+$ ,  $\text{Hg}^{++}$ ,  $\text{Pb}^{++}$ , and the larger alkaline earth salts are often insoluble. The  $\text{NH}_4^+$ ,  $\text{K}^+$ , and  $\text{Rb}^+$  salts of some of the most important heteropoly anions are insoluble, but these three cations form other soluble heteropoly salts. Salts of heteropolymolybdate and heteropolytungstate anions with cationic coordination complexes, alkaloids, or organic amines are usually insoluble. The albumins are coagulated and precipitated by most heteropolymolybdates and heteropolytungstates.

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; the hydrated salts are insoluble. Both 12-molybdophosphoric acid and its cobalt salt can be dissolved and recovered intact from molten benzoic acid solutions<sup>5)</sup>.

3. The crystalline free acids and salts of heteropolymolybdates and heteropolytungstate anions are almost always highly hydrated. A given acid or salt will often form several solid hydrates.

4. Many heteropoly compounds are highly colored, the colors ranging through the spectrum and occurring in many shades.

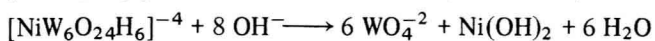
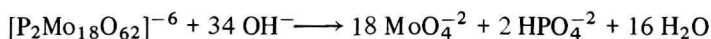
5. Some heteropoly compounds – and especially heteropolymolybdates – are strong oxidizing agents and can be very readily changed to fairly stable, reduced heteropolymolybdates. The reduction products are colored an intense deep blue. In solution the blue substances obey Beer's Law of Light Absorption. The reduced products can in turn act as reducing agents, and the original colors of the anions are restored on oxidation.

6. Recent work has shown that the free heteropolymolybdic acids are strong acids<sup>15)</sup>. The acids are always stronger than molybdic acid or the simple acid containing the central atom in a 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 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 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 and heteropolytungstate anions are decomposed by strongly basic solutions.

The final products are simple molybdate or tungstate ions and either an oxyanion or a hydrous metal oxide of the central 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. Heteropolytungstates are more stable in acid solutions than the corresponding molybdates. As a rule, heteropolytungstates are hydrolytically more stable than the heteropolymolybdates.

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

8. Throughout specific ranges of pH and other conditions, most solutions of heteropolymolybdates and heteropolytungstates 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 heteropoly anions are remarkably stable.

## Preparation

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

When the central atom is not a transition element, a soluble molybdate or tungstate may be dissolved with a soluble salt containing the central 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 central atom, or molybdenum trioxide is boiled with a solution containing the atom.

When the central atom is a transition metal, a simple salt of that element may be mixed hot with a soluble molybdate or tungstate in a solution of appropriate pH. If the central atom must be raised to an unusual oxidation state, persulfate, peroxide or bromine water are often employed; electrolytic oxidation may also be used. Alternatively, freshly precipitated hydrous metal oxides may be boiled in acidic molybdate or tungstate 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<sup>7, 19, 20</sup>;
4. by ion exchange from heteropoly salts<sup>7, 21</sup>;
5. from mixed or aprotic solvents<sup>7, 22</sup>.

A critical evaluation of preparative procedures of heteropoly compounds through 1970 has appeared<sup>7, 271</sup>. Valuable procedures for preparing phosphorus containing heteropoly compounds are given in Ref.<sup>23</sup>. Refs.<sup>8</sup>) and <sup>24-27</sup>) give procedures for numerous heteropoly compounds but they should be used with caution since some of these are not critical. An extensive review of the literature and references to the preparation of heteropoly compounds through 1955 may also be found in Ref.<sup>28</sup>). Preparations *via* non-ether routes for 12-molybdophosphoric and 12-molybdosilicic acid and several of their metal salts are given in Ref.<sup>5</sup>). Some pertinent comments on