chemists and 760 as physicists. Of the chemists 87% are members of the American Chemical Society, while only 2.5% belong also to the American Physical Society. Seventy-seven per cent. of the physicists are members of the American Physical Society, while 3.3% are also members of the American Chemical Society. Thus only about 3% of the physicists and chemists of the United States, whose names are given in the American Men of Science, belong to both of the national societies. This leaves far too small a number of men who are capable or are properly prepared to carry on the important work of bringing these two sciences closer together.

To pave the way for the coming revolutionary changes in chemistry we must be prepared to modify our methods of thinking, probably along lines now so prevalent in physics. But above all we must urge young chemists in the universities and after graduation to become thoroughly well trained in mathematics and in modern physics.

[Contribution from the Gates Chemical Laboratory, California Institute of Technology, No. 225]

THE MOLECULAR STRUCTURE OF THE TUNGSTOSILICATES AND RELATED COMPOUNDS

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1. Introduction

The molecular structure of the heteropolyacids[1] such as 12-tungstosilicic acid, $H_4SiW_{12}O_{40}\cdot xH_2O$, has long been the subject of speculation. A structure based upon Werner's coördination theory, suggested by Miolati,[2] has been developed and extensively applied in the systematization of heteropolyacids by Rosenheim,[3] and now is generally used in the discussion of these acids.[4] The Miolati-Rosenheim conception is, however, far from satisfactory. It provides no explanation for the characteristic properties of these acids and their salts, and the single definite pre-

[1] A historical summary of work on the heteropolyacids, with complete references to the papers of C. Marignac, F. Kehrmann, H. Copaux, W. Gibbs and many other investigators, is given by A. Rosenheim and J. Jaenicke, *Z. anorg. Chem.*, **100**, 304 (1917).

[2] A. Miolati, *J. prakt. Chem.*, [2] **77**, 417 (1908).

[3] (a) A. Rosenheim and co-workers, *Z. anorg. Chem.*, **69**, 247 (1910); (b) **69**, 261 (1910); (c) **70**, 73 (1911); (d) **70**, 418 (1911); (e) **75**, 141 (1912); (f) **77**, 239 (1912); (g) **79**, 292 (1913); (h) **84**, 217 (1913); (i) **89**, 224 (1914); (j) **91**, 75 (1915); (k) **93**, 273 (1915); (l) **96**, 139 (1916); (m) **100**, 304 (1917); (n) **101**, 215 (1917); (o) **101**, 235 (1917).

[4] F. Ephraim, "Inorganic Chemistry," Gurney and Jackson, London, **1926**, pp. 405–419; J. N. Friend, "A Textbook of Inorganic Chemistry," Griffin, London, **1926**, Vol. VII, Part III, pp. 251–268; etc.

diction which it makes, concerning the number of acid hydrogen atoms, is in disagreement with the results of experiment.

By applying the principles which have been found to underlie the formation of coördinated structures in crystals, I have deduced a structure which accounts for all of the characteristic properties of the heteropoly-acids; namely (1) the existence of a series of stable and eminently crystallizable compounds such as $H_4SiW_{12}O_{40}\cdot 31H_2O$ differing greatly in properties from the acids H_2WO_4, $H_2W_2O_7$, etc.; (2) the number of replaceable hydrogen atoms in these acids; (3) the number of molecules of water of crystallization in crystals of the acids and their salts; (4) the crystal form of the acids and their salts; and (5) the tendency of the 12-acids to condense to similar acids, such as $H_3PW_9O_{31}\cdot xH_2O$, in which the number of tungsten or molybdenum atoms per central atom is less than twelve; and which further leads to a number of predictions regarding the attributes of these substances which can be tested by means of the experiments that they suggest.

2. The Classification of the Molybdenum and Tungsten Polyacids. The Miolati-Rosenheim Theory

It was pointed out by Rosenheim[5] that there are two classes of heteropolyacids of molybdenum and tungsten, differentiated by their physical and chemical properties. Examples of the so-called 12-class are $H_4SiW_{12}O_{40}\cdot xH_2O$, $H_3PW_{12}O_{40}\cdot xH_2O$, etc.; of the 6-class $H_5I(MoO_4)_6$, etc. These acids, with 12 or 6 tungsten or molybdenum atoms per central atom, are called saturated 12-acids or 6-acids. Other members of each class exist in which the number of tungsten or molybdenum atoms per central atom is less than 12 or 6, respectively, but no well authenticated compound exists in which this ratio is greater than that for the saturated acids.

Copaux[6] prepared and analyzed a number of borotungstates, and observed the existence of isomorphism between borotungstates, silicotungstates, phosphotungstates and metatungstates, in the following cases

$5BaO\cdot B_2O_3\cdot 24WO_3\cdot 54H_2O$	Orthorhombic, pseudocubic
$6BaO\cdot 2H_2O\cdot 24WO_3\cdot 53$ or $54H_2O$[7]	
$4H_2O\cdot 24WO_3\cdot 53H_2O$	Trigonal, pseudocubic
$2H_2O\cdot 2SiO_2\cdot 24WO_3\cdot 50H_2O$	
$3H_2O\cdot P_2O_5\cdot 24WO_3\cdot 48H_2O$	
$6K_2O\cdot 2H_2O\cdot 24WO_3\cdot 37H_2O$	Hexagonal
$5K_2O\cdot B_2O_3\cdot 24WO_3\cdot 36H_2O$	
$4K_2O\cdot 2SiO_2\cdot 24WO_3\cdot 36H_2O$	
$6(NH_4)_2O\cdot 2H_2O\cdot 24WO_3\cdot 46H_2O$	Tetragonal, pseudocubic
$5(NH_4)_2O\cdot B_2O_3\cdot 24WO_3\cdot 52H_2O$	
$5H_2O\cdot B_2O_3\cdot 24WO_3\cdot 61H_2O$	

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[5] A. Rosenheim, *Z. anorg. Chem.*, **96**, 139 (1916).

[6] H. Copaux, *Ann. chim. phys.*, [8] **17**, 217 (1909).

[7] See H. Copaux, *Z. anorg. Chem.*, **74**, 351 (1912). The exact water content of some of these substances is doubtful.

In addition he formed a series of solid solutions between potassium metatungstate and potassium silicotungstate. As a result of these observations he concluded that the metatungstates are to be considered as 12-tungstoacids in which water plays the role of the central group.

Rosenheim and Felix[8] similarly classified the tetra- and octomolybdates as 12-molybdates.

Salts representative of the 12-class and 6-class are tabulated below.

12-class		6-class	
$K_6H_2W_{12}O_{40}\cdot 18\frac{1}{2}H_2O$	$K_3PW_9O_{31}\cdot 7H_2O$	$K_5I(MoO_4)_6$	$K_3H_6R^{+3}(MoO_4)_6$
$K_5BW_{12}O_{40}\cdot 18H_2O$	$K_4SiMo_{12}O_{40}\cdot 18H_2O$	$K_6Te(MoO_4)_6$	$R^{+3} = Al^{+3}, Fe^{+3}$
$K_4SiW_{12}O_{40}\cdot 18H_2O$	$K_3AsMo_9O_{31}\cdot 14H_2O$	$K_4H_6Ni(MoO_4)_6$	Cr^{+3}, Mn^{+3}
$Na_3PW_{12}O_{40}\cdot 21H_2O$	etc.	$K_3AsO(MoO_4)_3$	etc.

The members of the 12-class are all similar to metatungstates; the free acids are easily prepared, very stable, and very easily crystallizable. The molybdenum compounds are almost without exception deep yellow in color. The members of the 6-class, on the other hand, show the reactions of the molybdate or tungstate ion, $[MoO_4]^{--}$ or $[WO_4]^{--}$. The molybdates are colorless when the central ion is colorless.

There is no doubt that Rosenheim has assigned the correct structures to the members of the 6-class. The complex anions are composed of MoO_4 or WO_4 tetrahedra. By sharing one corner, two of these tetrahedra form the ion $[Mo_2O_7]^{--}$, etc. By sharing a corner of each MoO_4 tetrahedron with the AsO_4 group, the ions $[AsO_3(MoO_4)]^{-3}$, $[AsO_2(MoO_4)_2]^{-3}$, $[AsO(MoO_4)_3]^{-3}$, $[As(MoO_4)_4]^{-3}$ may be formed. Similarly a central ion with coördination number of six can form an octahedron, all six corners of which may be shared with MoO_4 tetrahedra.

The Miolati-Rosenheim conception of the 12-acids is that they are similarly derived from the central groups $[H_2O_6]^{-10}$, $[BO_6]^{-9}$, $[SiO_6]^{-8}$, $[PO_6]^{-7}$, etc., by replacing the oxygen atoms by Mo_2O_7 or W_2O_7 groups. The corresponding acids are then written $H_{10}[H_2(W_2O_7)_6]$, metatungstic acid; $H_9[B(W_2O_7)_6]$, 12-tungstoboric acid; $H_8[Si(W_2O_7)_6]$, 12-tungstosilicic acid; $H_7[P(W_2O_7)_6]$, 12-tungstophosphoric acid; and similarly for the 12-molybdoacids. But the acids do not have the large number of replaceable hydrogen atoms indicated by these formulas. Their salts indicate that the true basicities are four less than this. Very many neutral salts corresponding to the formulas $H_6[H_2W_{12}O_{40}]\cdot xH_2O$, $H_5[BW_{12}O_{40}]\cdot xH_2O$, $H_4[SiW_{12}O_{40}]\cdot xH_2O$ and $H_3[PW_{12}O_{40}]\cdot xH_2O$ have been prepared, but only a few salts in which four more hydrogen atoms are replaced. These formulas, accepted by most investigators in this field,[9] no doubt represent correctly the number of replaceable hydrogen atoms, so that the Miolati-Rosenheim theory leads to incorrect results in this

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[8] A. Rosenheim and J. Felix, *Z. anorg. Chem.*, **79**, 292 (1913).

[9] H. Copaux, *ibid.*, **74**, 351 (1912); F. Kehrmann, *ibid.*, **39**, 98 (1904); G. Wyrouboff, *Bull. soc. franc. min.*, **28**, 239 (1905); etc.

respect. Rosenheim has contended that the ordinary salts are really acid salts, and he did succeed in replacing seven hydrogen atoms in 12-molybdophosphoric acid and 12-tungstophosphoric acid with guanidine. In other cases, however, guanidine replaces fewer hydrogen atoms than correspond to the Miolati-Rosenheim theory, so that the theory is not supported. Some salts of heavy metals also are known in which more hydrogen atoms are replaced than in the ordinary salts; these we consider to be basic salts.

The Miolati-Rosenheim theory offers no explanation of the characteristic properties of the 12-acids; for it involves the coördination about a central atom of six Mo_2O_7 or W_2O_7 groups, which are evidently identified with the bimolybdate and bitungstate ions, $[Mo_2O_7]^{--}$ and $[W_2O_7]^{--}$, and are hence composed of two MoO_4 or WO_4 tetrahedra with one corner shared. Accordingly they would be expected to show the reactions of the $[MoO_4]^{--}$ or $[WO_4]^{--}$ ion, and to belong to the same class as the 6-acids. In order to account for the pronounced differences between the 12-acids and the 6-acids there is needed a radical difference in structure, and this is not provided by the Miolati-Rosenheim theory.

3. The Structure of the 12-Tungstosilicate Ion and Related Ions

A set of principles underlying the formation of coördinated structures in crystals has been formulated and discussed in a previous paper.[10] These principles are also applicable in general to atom groups of finite extent. The following discussion illustrates their use in the deduction of the structures of highly complex ions.

Molybdenum and tungsten form tetrahedral ions, $[MoO_4]^{--}$ and $[WO_4]^{--}$, in which they have a coördination number of four. (It is probable that the metal–oxygen bonds in these ions are all of the shared electron pair type.) But the crystal radii[11] of the ions Mo^{+6} and W^{+6} are both about 0.62 Å., so that it is possible to group six oxygen ions, of crystal radius 1.35–1.40 Å., about one ion Mo^{+6} or W^{+6} at octahedron corners (Fig. 1). It is to be expected, then, that such an arrangement will also occur; and it has actually been shown to exist[12] in crystals of ammonium oxyfluomolybdate, $(NH_4)_3MoO_3F_3$, in which three oxygen ions and three fluorine ions are grouped about each molybdenum ion.

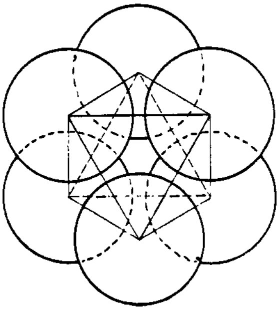

Fig. 1.—Six oxygen ions arranged at the corners of a regular octahedron about a tungsten or molybdenum ion.

Stable complexes may then be formed by arranging MoO_6 or WO_6 octahedra in such a way that they share corners with each other. The

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[10] Linus Pauling, This Journal, **51**, 1010 (1929).

[11] Linus Pauling, *ibid.*, **49**, 765 (1927).

[12] Linus Pauling, *ibid.*, **46**, 2738 (1924).

strength of the electrostatic bond from a hexavalent cation[13] to each corner of the octahedron of anions about it is 1, so that each oxygen ion will tend to be shared between two octahedra. On account of the large electric charge of the cations, the octahedra will share corners only, and not edges or faces.

A structure satisfying these requirements is shown in Fig. 2. Each octahedron shares three corners with adjoining octahedra, and has three unshared corners. The double negative charge of the oxygen ions at the unshared corners is not satisfied by the single molybdenum or tungsten electrostatic bond, of strength 1; in order that it be satisfied, each of these 36 oxygen ions must take up a hydrogen ion. The resultant $Mo_{12}O_{18}(OH)_{36}$ group is electrically neutral.

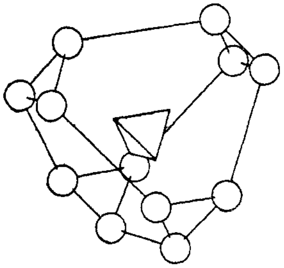

Fig. 2a.—Diagrammatic representation of a structure composed of twelve tungsten or molybdenum octahedra. Each octahedron is replaced by a circle. The lines connecting circles indicate that the corresponding octahedra are united through the possession of a common corner (an oxygen bond).

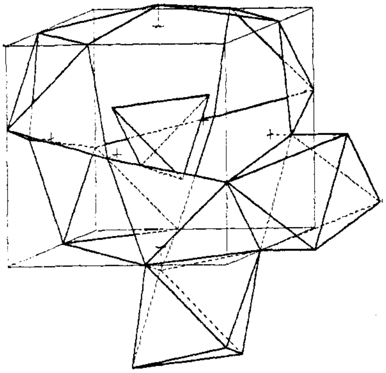

Fig. 2b.—The structure composed of twelve octahedra. Two octahedra are completely drawn. The face defined by the shared corners is shown for each of the others.

As a result of the strong repulsion between the adjacent highly charged cations the octahedra composing the group will be distorted. The distortion will take place in such a way that the Mo–O or W–O distance will remain approximately constant. The oxygen–oxygen distance determining the length of an octahedron edge is usually 2.70–2.80 Å., but may be as small as 2.50 Å. The mutual repulsion of the molybdenum or tungsten ions in the structure we are discussing will lengthen the three edges of each octahedron determined by the shared corners, the other edges being correspondingly shortened. In the crystals in which octahedron edges are shortened to 2.50 Å. (rutile, brookite, anatase, corundum),

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[13] Throughout this paper use will be made of the word ion, although it is recognized that the bonds may not approach the limiting case of purely ionic bonds very closely.

four edges at the most are so affected. In the MoO_6 and WO_6 octahedra nine edges are shortened by deformation, so that all of the oxygen ions are brought close together; it is probable that these nine edges will not be shorter than about 2.60 Å. If the metal–oxygen distances remain 2.00 Å. throughout, the other three edges are then about 3.10 Å. long, and the distorted octahedron has the appearance shown in Fig. 3.

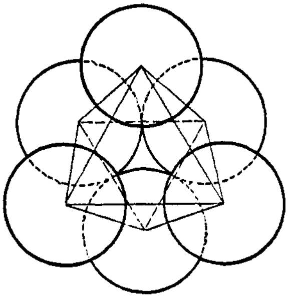

Fig. 3.—The distorted octahedron of oxygen ions about a tungsten or molybdenum ion.

As a result of this deformation, an additional oxygen ion at one corner of the tetrahedron of Fig. 2 would be reasonably close to three molybdenum or tungsten ions; in fact, if it remained at a distance of about 2.7 Å. from the oxygen ions at the shared corners of the octahedra, it would be about 3.0 Å. from the three metal ions, each of charge +6. These positions, in regions of positive potential, are accordingly stable ones for oxygen ions.

It is also to be anticipated that the position in the region of negative potential at the center of the tetrahedron formed by these four oxygen ions would be stable for a small positive ion, such as B^{+3}, Si^{+4}, P^{+5}, As^{+5}, etc., with crystal radii 0.21, 0.41, 0.34 and 0.47 Å., respectively. For the strength of the electrostatic bond from Mo^{+6} or W^{+6} at the distance 3.0 Å. may be about $^1/_2$, in which case the three metal ions would not satisfy the charge of the oxygen ion and another positive ion would be required. If no other positive ion is available for this purpose, hydrogen ions would be used. The experimental observation that metatungstic acid is hexabasic indicates that two hydrogen ions are required for the four oxygen ions.

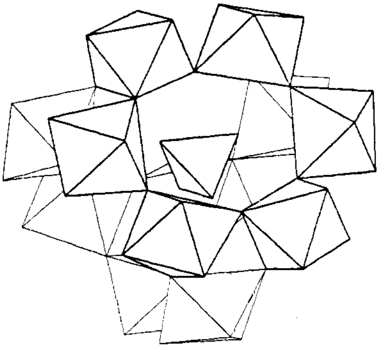

Fig. 4.—The structure of the 12-tungstosilicate ion and related ions. Twelve distorted octahedra (Fig. 3) are combined by sharing corners as shown. The tetrahedron represents the $[SiO_4]^{-4}$ ion. The complete structure has the composition $[SiO_4 \cdot W_{12}O_{18}(OH)_{36}]^{-4}$, and has the point-group symmetry T_d.

The completed complex ion, shown in Fig. 4, can now be described in the following way. Twelve molybdenum or tungsten octahedra combine by sharing corners occupied by oxygen ions (eighteen altogether). Each of the thirty-six unshared oxygen ions takes up a hydrogen ion to satisfy its negative charge. The resultant neutral structure is then stabilized by a central tetrahedral group $[RO_4]^{-3}$, with R = H_2^{++}, B^{+3}, Si^{+4}, P^{+5}, As^{+5}, etc. The central stabilizing group increases the stability of the complex not only by introducing negative ions in regions of large positive potential, but also by completing a structure which approximates close-packing of the large ions, each of the central oxygen ions being in contact with nine oxygen ions.

A first test of the possibility of existence of this structure is the investigation of the dimensions of the group of twelve octahedra to determine whether or not there is room for an RO_4 group within. In the $[SiO_4]^{-4}$ ion the oxygen–oxygen distance is about 2.60 Å., the silicon–oxygen distance being about 1.59 Å.[14] The $[BO_4]^{-5}$, $[PO_4]^{-3}$ and $[AsO_4]^{-3}$ ions have about the same dimensions. Assuming three edges of each octahedron to be lengthened to 3.10 Å., each oxygen ion of the central RO_4 group will be about 2.85 Å. from six oxygen ions in the surrounding structure. There is accordingly just room enough for the central tetrahedron. *A structure composed of less than twelve octahedra could not be built about the* RO_4 *group.*

A study of the structure has led to the conclusion that the deformation of the octahedra is not so great as that estimated to be the maximum possible. The nine short edges are probably about 2.65 Å., and the three long edges about 3.02 Å. long. Each RO_4 oxygen ion is then about 2.77 Å. from six oxygen ions of the surrounding structure, and about 3.14 Å. from three W^{+6} or Mo^{+6} ions. The corresponding atomic positions are given by the following set of coördinates relative to orthogonal axes

1Si, B, P or As at 0 0 0
$4O_I$ at $u\,u\,u$, $u\,\bar{u}\,\bar{u}$. $\bar{u}\,u\,\bar{u}$, $\bar{u}\,\bar{u}\,u$, with u = 1.59 Å.
$6O_{III}$ at $t\,0\,0$, $0\,t\,0$, $0\,0\,t$, $\bar{t}\,0\,0$, $0\,\bar{t}\,0$, $0\,0\,\bar{t}$, with t = 3.37 Å.
$12O_{II}$ at $v\,v\,w$, $v\,\bar{v}\,\bar{w}$, $\bar{v}\,v\,\bar{w}$, $\bar{v}\,\bar{v}\,w$
$v\,w\,v$, $v\,\bar{w}\,\bar{v}$, $\bar{v}\,w\,\bar{v}$, $\bar{v}\,\bar{w}\,v$
$w\,v\,v$, $w\,\bar{v}\,\bar{v}$, $\bar{w}\,v\,\bar{v}$, $\bar{w}\,\bar{v}\,v$
with v = 2.88 Å. and w = 0.74 Å.

$12O_{IV}$ at v v w, etc., with v = 2.55 Å. and w = 4.80 Å.
12W or Mo at v v w, etc., with v = 1.35 Å. and w = 4.00 Å., about
$24O_{IV}$ at $x\,y\,z$, $z\,x\,y$, $y\,z\,x$, $y\,x\,z$, $x\,z\,y$, $z\,y\,x$
$x\,\bar{y}\,\bar{z}$, $z\,\bar{x}\,\bar{y}$, $y\,\bar{z}\,\bar{x}$, $y\,\bar{x}\,\bar{z}$. $x\,\bar{z}\,\bar{y}$, $z\,\bar{y}\,\bar{x}$
$\bar{x}\,y\,\bar{z}$. $\bar{z}\,x\,\bar{y}$, $\bar{y}\,z\,\bar{x}$, $\bar{y}\,x\,\bar{z}$, $\bar{x}\,z\,\bar{y}$, $\bar{z}\,y\,\bar{x}$
$\bar{x}\,\bar{y}\,z$, $\bar{z}\,\bar{x}\,y$, $\bar{y}\,\bar{z}\,x$, $\bar{y}\,\bar{x}\,z$, $\bar{x}\,\bar{z}\,y$, $\bar{z}\,\bar{y}\,x$
with x = 0.02 Å., y = 5.28 Å., and z = 1.90 Å.

4. The Properties of the 12-Tungsto- and Molybdoacids

The structure proposed for the 12-tungsto- and molybdoacids, in which the tungsten and molybdenum atoms have a coördination number of six, requires, in agreement with experiment, that these substances have

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[14] These distances are in agreement with those found experimentally for orthosilicates.

distinctly different properties from the ordinary tungstic and molybdic acids, with coördination number four.

Formulas for the tungsten acids corresponding to the proposed structure are

$H_6[H_2O_4 \cdot W_{12}O_{18}(OH)_{36}]$, metatungstic acid
$H_5[BO_4 \cdot W_{12}O_{18}(OH)_{36}]$, 12-tungstoboric acid
$H_4[SiO_4 \cdot W_{12}O_{18}(OH)_{36}]$, 12-tungstosilicic acid
$H_3[PO_4 \cdot W_{12}O_{18}(OH)_{36}]$, 12-tungstophosphoric acid

Similar formulas are to be ascribed to the molybdenum acids. *The numbers of replaceable hydrogen atoms given by these formulas are exactly those found experimentally.* This is a consequence of the fact that the coördinated structure surrounding the central RO_4 group is electrically neutral, so that the complex anion has the same charge as the RO_4 group itself; in other words, the heteropolyacid has the same number of replaceable hydrogens as the acid from which it was derived.

A further notable feature of the proposed structure is the large amount of water of constitution, amounting to $18H_2O$ per molecule, aside from the replaceable hydrogen of the acids and the central hydrogen of the metatungstates and the corresponding molybdates. This explains the high water content characteristic of these compounds, which had long been an unsolved puzzle. The water content of the heteropolyacids was studied by Rosenheim and Jaenicke,[3f] who found the results given in Table I. There is some doubt as to the exact amount of water in many cases; for example, previous investigators had assigned $31H_2O$ to the series of crystals corresponding to the first column, instead of $30H_2O$.

TABLE I

WATER CONTENTS OF HETEROPOLYACIDS

$H_6[H_2W_{12}O_{40}]$	..	$24H_2O$	14–17 H_2O (?)
$H_5[BW_{12}O_{40}]$	$30H_2O$	$\boxed{24}$	12
$H_4[SiW_{12}O_{40}]$	30	24	$\boxed{22}$
$H_3[PW_{12}O_{40}]$	30	24	21
$H_4[SiMo_{12}O_{40}]$	30	..	14
$H_3[PMo_{12}O_{40}]$	30	24	14 (?)

The 30- and 24-hydrates are compatible with our formulas. We would say that eighteen molecules of water is water of constitution, and that $12H_2O$ or $6H_2O$ only is water of crystallization, that is, water which fills the interstices which result from piling together the large constituent groups in the construction of the crystals. It is to be expected that usually there will be some water of crystallization, on account of the shape of the complex anions.

Four[15] of the hydrates of the third column contain less than $18H_2O$.

[15] Two of these could not be identified with certainty as distinct compounds.

These substances are, however, different from the others in their properties. Rosenheim and Jaenicke state that they dehydrate on heating without melting, whereas the others show definite melting points. They can be prepared only under dehydrating conditions—by crystallizing out of concentrated nitric acid, or by heating the higher hydrates to constant weight at temperatures above their melting points. These properties are to be expected from the proposed structure, assuming that dehydration consists in the sharing of corners between octahedra in different complexes, with the elimination of $1H_2O$ for each shared corner. The coördination bonds introduced between the complexes in this way tie the whole crystal together, and prevent it from melting at a low temperature. The presence of compounds with over $18H_2O$ in this column is not surprising; they contain less than 18 molecules of water of constitution, and in addition some water of crystallization.

The 30-hydrates are all isomorphous, and so are the 24-hydrates, with the exception of the tungstoboric acid. This tungstoboric acid and the tungstosilicic acid of the third column are isomers of the ordinary heteropolyacids; their structure is discussed in the following section.

The existence of 18 molecules of water of constitution is further indicated by the data on salts, most of which crystallize with $18H_2O$ or more. For example, Groth[16] lists seventy-seven salts of 12-tungstosilicic acid which have been subjected to crystallographic examination. Of these all but thirteen contain $18H_2O$ or more, the exceptional ones having $13–17H_2O$.

The 12-heteropolyacids and their salts have a pronounced tendency to form cubic or pseudocubic crystals; thus about two-thirds of the 12-tungstosilicates with $18H_2O$ or more are cubic or pseudocubic (Table II), and the other acids and their salts crystallize similarly. The structure proposed for these complex anions has the symmetry of the cubic point-group T_d. Accordingly cubic crystals of simple structure, containing as little as one complex anion in the unit of structure, can be built of these groups, and such crystals would be expected to occur. If, on the other hand, the complex anion did not possess cubic symmetry, a very large unit of structure would be required in a cubic crystal, and these crystals would be the exception and not the rule. It is also significant that salts with less than $18H_2O$ are all triclinic or monoclinic and show no pseudocubic development. Further similar evidence for 18 molecules of water of constitution and for the cubic point-group symmetry of the complex anions is provided by the three tungstophosphates listed by Groth.[17] The salt with less than $18H_2O$, $Na_3PW_{12}O_{40}\cdot 15H_2O$, is triclinic, while $Na_3PW_{12}O_{40}\cdot 21H_2O$ and $Ba_3(PW_{12}O_{40})_2\cdot 48H_2O$ form cubic crystals.

[16] Groth, "Chemische Kristallographie," Engelmann, Leipzig, 1908, Vol. II.

[17] Groth, Ref. 16, Vol. II, pp. 883–884.

TABLE II

CRYSTALLINE FORM OF 12-TUNGSTOSILICATES

No.		
1	Triclinic or monoclinic	$Na_4X\cdot 20H_2O$ ($X = [SiW_{12}O_{40}]^{-4}$)
		$R_2X\cdot 18H_2O$; R^{+2} = Ca, Mg, Mn, Ni, Co, Zn
		$Pb_2X\cdot 21H_2O$ $Sr_2X\cdot 23H_2O$
		$Cd_2X\cdot 22H_2O$ $InHX\cdot 20H_2O$
		$R_4X_3\cdot 60H_2O$; R^{+3} = Al, Cr, Ga, Bi
		$In_4X_3\cdot 63H_2O$
		$RHX\cdot 18H_2O$; R^{+3} = La, Ce, Di, Gd
		$RHX\cdot 24\frac{1}{2}H_2O$; R^{+3} = Y, Tb, Yb
2	Hexagonal—$a:c$ = 1:0.6585	$K_4X\cdot 18H_2O$
3	Tetragonal—$a:c$ = 1:1.0117 (pseudocubic)	$H_4X\cdot 30$ or $31H_2O$
4	Trigonal—α = 86° 26′–89° 8′ (pseudocubic)	$Li_4X\cdot 24H_2O$
		$R_2X\cdot 24H_2O$; R^{+2} = Ca, Ba
		$H_4X\cdot 24H_2O$
5	Trigonal[a]—α = 75° 43′–77° 18′	$R_4X_3\cdot 78H_2O$; R^{+3} = Nd, Di, Sm, Gd, Y, Tb, Yb
6	Trigonal—α = 56° 4′–57° 30′ (pseudocubic)	$R_2X\cdot 27H_2O$; R^{+2} = Ca, Sr, Mg, Mn, Ni, Co, Cu, Zn, Cd
		$Be_2X\cdot 29H_2O$
		$R_4X_3\cdot 87H_2O$; R^{+3} = Al, Cr, Ga
		$R_4X_3\cdot 81H_2O$; R^{+3} = La, Ce, Di, Sm, Gd
		$Gd_4X_3\cdot 90H_2O$ $ThX\cdot 27H_2O$ $ThX\cdot 30H_2O$
7	Cubic	$Be_2X\cdot 31H_2O$
		$R_4X_3\cdot 93H_2O$; R^{+3} = Al, Cr, Fe, Ga, In

[a] These crystals, while not pseudocubic in their face development, have axial ratios in the neighborhood of 1:3, and so may have a pseudocubic structure.

5. Iso-12-Tungstosilicic Acid and Iso-12-Tungstoboric Acid

There exist in addition to the 12-acids just discussed acids of the composition $H_4(SiW_{12}O_{40})\cdot xH_2O$ and $H_5(BW_{12}O_{40})\cdot xH_2O$ which differ from them in their reactions, and are called iso-12-acids. Iso-12-tungstosilicic acid and its salts were discovered and investigated by Marignac.[18] Iso-12-tungstoboric acid, previously studied by Copaux,[19] was assigned its accepted formula and further studied by Rosenheim.[20] The iso-acids retain their identity on solution and recrystallization, and on conversion into salts and again into acids. They are prepared by heating solutions of the normal acids to dryness and are also formed to some extent in the preparation of the normal acids and their salts.

The Miolati-Rosenheim theory[21] has been made to account for the existence of two forms of 12-tungstosilicic and 12-tungstoboric acid by

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[18] C. Marignac, *Ann. chim. phys.*, [4] **3**, 5 (1864).

[19] H. Copaux, *ibid.*, [8] **17**, 217 (1909).

[20] A. Rosenheim, *Z. anorg. Chem.*, **70**, 418 (1911); A. Rosenheim and J. Jaenicke, *ibid.*, **101**, 235 (1917).

[21] A. Rosenheim and J. Jaenicke, *ibid.*, **100**, 304 (1917); P. Pfeiffer, *ibid.*, **105**, 26 (1918).

assuming a difference in character of some of the six positions about the central atom and the others.

The method of formation of the iso-acids by heating the normal acids suggests a condensation of the normal complex anions with the liberation of water of constitution. The ease of solution and reprecipitation of the iso-acids requires that the constituent coördinated groups be not too large. A structure satisfying these requirements is obtained by combining two $[RO_4W_{12}O_{18}(OH)_{36}]^{-z}$ groups in such a way that six octahedra of one group share one corner apiece with six octahedra of the other group. The resultant anion is shown in Fig. 5. The acids would then have the formulas

$$H_8[(SiO_4)_2W_{24}O_{42}(OH)_{60}] \text{ or } H_4[SiW_{12}O_{40}]\cdot 15H_2O$$
$$H_{10}[(BO_4)_2W_{24}O_{42}(OH)_{60}] \text{ or } H_5[BW_{12}O_{40}]\cdot 15H_2O$$

The amount of water of constitution, $15H_2O$, required by this structure is compatible with the observed hydration of the acids, $24H_2O$ and $22H_2O$ (Table I), for it is to be expected that some water of crystallization will also be present.

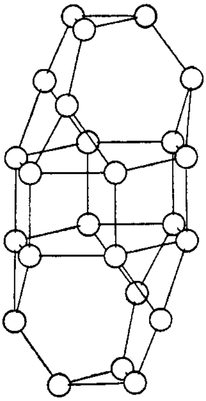

Fig. 5a.

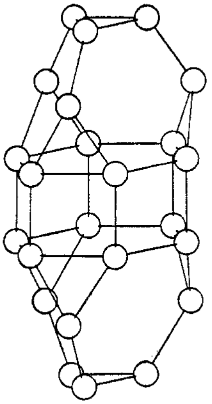

Fig. 5b.

Fig. 5a.—A possible structure for the iso-12-polyacid ion, made from two ions of Fig. 4 by the elimination of $6H_2O$ and the formation of six oxygen bonds. Point-group symmetry D_{3d}.

Fig. 5b.—The probable structure of the iso-12-polyacid ion. Point-group symmetry D_{3h}.

The salts of these acids also usually crystallize with over $15H_2O$. The well-investigated crystals $K_4SiW_{12}O_{40}\cdot 9H_2O$ (rhombic) and $Na_4SiW_{12}O_{40}\cdot 12H_2O$ (trigonal) are exceptions. It is probable that further dehydration, with the accompanying sharing of octahedron corners between the iso-anions, has taken place here.

The iso-anion $[(RO_4)_2W_{24}O_{42}(OH)_{60}]^{-2z}$ has the symmetry of the point-group D_{3d} (Fig. 5a), or, more probably, D_{3h} (Fig. 5b). Verification of the proposed structure will be attempted through the investigation with x-rays of the hexagonal bipyramidal crystals of iso-12-tungstoboric acid, $H_5[BW_{12}O_{40}]\cdot 24H_2O$.

6. The Unsaturated or Condensed Heteropolyacids

There also exist heteropolyacids, similar in their reactions to the saturated 12-heteropolyacids, in which the number of tungsten or molybdenum atoms per central atom is less than twelve. It is probable that the anions of these acids are formed from the 12-anions by the sharing between two groups of some complete octahedra. The 12-octahedra groups are of such a nature that two can combine by sharing six octahedra, as shown in Fig. 6, or by sharing two octahedra.

The acids formed from the 12-acids of phosphorus or arsenic would have formulas of the type

$$H_6[(PO_4)_2W_{18}O_{30}(OH)_{48}] \text{ or } H_6[P_2W_{18}O_{62}]\cdot 24H_2O$$

These acids should then have six replaceable hydrogen atoms and contain 24 molecules of water of constitution.

Phosphorus and arsenic form 9-acids with both molybdenum and tungsten very easily.[22] (It is, indeed, reported to be difficult to prepare salts of the saturated arsenic acids, and the acids themselves are unknown.) Most of the salts of these acids are formed by replacing six hydrogen atoms, although in a few twelve hydrogen atoms are replaced. The basicity of the acids accordingly agrees with the structure suggested.

The crystallized free acids, of composition $H_6[P_2W_{18}O_{62}]\cdot 39H_2O$, $H_6[As_2W_{18}O_{62}]\cdot 39H_2O$, $H_6[P_2Mo_{18}O_{62}]\cdot 33$ or $37H_2O$ and $H_6[As_2Mo_{18}O_{62}]\cdot 25$ or $29H_2O$, all possess some water of crystallization in addition to the water of constitution. This is true also of a majority of the salts; in the exceptional cases the amount of constitutional water is diminished by the sharing of corners of octahedra in different complex anions.

The anions of formula $[(PO_4)_2W_{18}O_{30}(OH)_{48}]$, etc., have the symmetry of the point-group D_{3d}. Verification of this should be possible through the examination with x-rays of the dihexagonal bipyramidal crystals $K_6P_2W_{18}O_{62}\cdot 28H_2O$, $K_6As_2Mo_{18}O_{62}\cdot 28H_2O$ and $Na_6As_2Mo_{18}O_{62}\cdot 30H_2O$.[23]

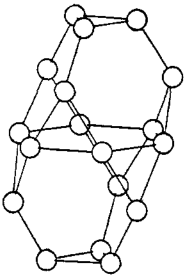

Fig. 6.—The probable structure of the 9-polyacid ion, formed from two ions of Fig. 4 by the sharing of six octahedra. Point-group symmetry D_{3d}. The structure of point-group symmetry D_{3h} (the analog of Fig. 5b) is probably unstable.

It is possible that each anion of the compounds with 11:1 as the ratio of the number of molybdenum or tungsten atoms to the number of central atoms is formed from two 12-anions with two octahedra in common, and that the anions of the compounds reported with ratios 10:1, 21:2 and 17:2 are composed of more than two 12-anions combined by sharing octahedra. In these cases, however, the confident assignment of specific structures must follow further experimental investigation.

Summary

There is described a structure for the 12-heteropolyacids of molybdenum and tungsten derived by the application of the principles under-

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[22] A. Rosenheim and J. Jaenicke, *Z. anorg. Chem.*, **101**, 235 (1917); A. Rosenheim and A. Traube, *ibid.*, **91**, 74 (1915).

[23] Groth, Ref. 16, Vol. II, p. 879.

lying the formation of coördinated structures in complex crystals. The proposed structure, shown in Fig. 4, may be represented by formulas such as $H_4[SiO_4 \cdot W_{12}O_{18}(OH)_{36}]$. It correlates the characteristic differences between the properties of the 12-molybdo- and tungsto-acids and those of the $[MoO_4]^{--}$ and $[WO_4]^{--}$ ions with the existence of molybdenum and tungsten atoms with coördination numbers 6 and 4, respectively, in these two types of compounds. It leads to a number of replaceable hydrogen atoms in agreement with experiment, and accounts for the large water content of the acids and their salts. The cubic point-group symmetry of the suggested structure for the complex anions explains the tendency of these compounds to form cubic or pseudocubic crystals.

The iso-12-tungstosilicate and iso-12-tungstoborate ions are ascribed the structure shown in Fig. 5, in which two 12-anions are combined through the formation of oxygen bonds.

A structure for one class of unsaturated acids, corresponding to formulas such as $H_6[(PO_4)_2 \cdot W_{18}O_{30}(OH)_{48}]$, is also suggested, involving the combination of two 12-anions as shown in Fig. 6. Possible structures for other unsaturated acids are indicated.

Among the predictions made on the basis of the proposed structure and susceptible to experimental investigation are the following: that the normal 12-anions have the point-group symmetry T_d, and the iso-12-anions and the 9-anions the symmetry D_{3d} or D_{3h}; that the normal 12-acids have a molecular weight corresponding to one RO_4 group per complex, and the iso-12-acids and 9-acids to two; and that the constituent atoms in the complexes occupy certain positions relative to each other, such that each tungsten or molybdenum atom has a first coördination shell of six oxygen atoms none of which is part of the central RO_4 group.

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[CONTRIBUTION FROM THE CHEMICAL AND PHYSICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

THE CRYSTAL STRUCTURE OF META-IODOBENZOIC ACID[1]

BY HAROLD P. KLUG, EDWARD MACK, JR., AND F. C. BLAKE

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We have been led to an x-ray examination of the crystals of a number of benzene derivatives in connection with a study of vapor pressures and heats of vaporization. It seems worth while at this time to report the crystal structure which we have found for *m*-iodobenzoic acid, especially since the solution obtained seems to be unique, and very few unambiguous solutions have been reported for organic compounds crystallizing in the

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[1] An abstract of a thesis presented by H. P. Klug in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the Ohio State University in June, 1928.