THE CRYSTAL STRUCTURE OF ANHYDROUS SILICOTUNGSTIC ACID[1] AND RELATED COMPOUNDS, AND THEIR PROBABLE MOLECULAR FORMULAS

By Arthur G. Scroggie[2] and George L. Clark

Department of Chemistry, University of Illinois

Communicated November 19, 1928

Silicotungstic acid crystallizes in a number of forms with different amounts of water of hydration. It occurs as octahedrons with the following composition, $2H_2O.SiO_2.12WO_3.30H_2O$ and as rhombohedrons, $2H_2O.SiO_2.12WO_3.24H_2O$. An isomeric triclinic form with 22 molecules of water of hydration has been described, and also one containing 17 molecules of water of hydration, but the anhydrous acid obtained by heating the hydrated forms to a temperature of 220°, is obtained as a fine powder and its crystal structure has not been satisfactorily determined by optical means.

The arrangement of the atoms in the molecule has been the subject of speculation by Rosenheim, Asch and Asch, and others,[3] but the evidence offered has not been conclusive in any case.

The aim of the present research was to make an x-ray diffraction analysis of the crystal structure of silicotungstic acid and to combine these results with chemical data in an attempt to deduce the correct molecular structure, and to compare these results with previously suggested structures.

1. *Investigation of the Structure of the Acid.*—A. Chemical Examination. In this part of the work, the classical method of degrading the molecule and isolating and identifying the decomposition products was applied to silicotungstic acid. The acid was decomposed by an excess of KOH which causes the splitting off of molecules of K_2WO_4. These could be detected since they gave a yellow to white precipitate of WO_3, in the presence of strong mineral acids. The amount of acid necessary to cause the splitting of the acid molecule was established experimentally as follows: a series of solutions were prepared containing a known amount of acid, and a volume of KOH solution equal to 8, 9, 10, 11, 12, or 14 equivalents of alkali was added; after hydrolysis had reached an equi-

librium, the solutions were tested for K_2WO_4 by the addition of concentrated hydrochloric acid.

No precipitate could be obtained after the addition of 8, 9 or 10 equivalents of alkali, but one formed slowly in the solution to which 11 equivalents had been added, and an immediate precipitate was obtained from the solution containing 12 equivalents of base. These results indicated that the molecule of silicotungstic acid was split only when 11 or more equivalents of base were added, and proved experimentally that it was possible to prepare a salt containing eight basic equivalents without decomposing the acid, a possibility denied by Brauer and Flürscheim.[4]

The amount of WO_3 formed could not be determined exactly since it is not quantitatively precipitated under these conditions, but by filtering off the precipitate and extracting with ether and hydrochloric acid, various modified silicotungstic acids could be obtained. In general, very limited amounts of these acids were prepared in a pure state, but determinations of the neutral equivalent (N. E.) and the percentage of anhydride gave the following results.

	ANHYDRIDE	N. E.
A. After adding 14 equivalents of alkali:		
Experimental values (average)	95.01%	616
Theory for $2H_2O.SiO_2.10WO_3.5H_2O$	94.96	627
B. After adding 18 equivalents:		
Experimental values	94.67%	502
Theory for $2H_2O.SiO_2.8WO_3.4H_2O$	94.65	506
C. After adding 20 equivalents:		
Experimental values	95.22%	595
Theory for $3H_2O.(SiO_2.7WO_3)_2.4H_2O$	94.90	591

The formulas given correspond to the composition of the acids when dried at 100°. Acid A is well known as silicodecitungstic acid, and is regularly prepared by boiling silicotungstic acid with a slight excess of ammonia, and recrystallizing the barium salts. Acid B, silicoöctatungstic acid, and acid C, silicoheptatungstic acid, have not been previously described as decomposition products, though Rosenheim[5] has reported a salt of the latter prepared by synthetic methods. It was not found possible to isolate an acid with less than 7 atoms of tungsten when using the same methods. The decomposition products, therefore, indicate a comparatively stable molecular nucleus containing at least seven tungsten atoms, and the probability that the splitting off of the sixth tungsten atom causes a complete disintegration of the molecule.

B. X-ray Examination. An analysis of the acid dried at 100° using the powder method on a General Electric Diffraction Apparatus showed that silicotungstic acid, $4H_2O.SiO_2.12WO_3.4H_2O$, crystallizes as a body-centered cube. Lines corresponding to the following interplanar dis-

tances were measured with spectrograms of pure NaCl and tungsten wire
as calibration.   (See Plate 1.)

PLANE	$(h_2 + k_2 + l_2)$	INTERPLANAR DISTANCE	INTENSITY	LOG. a_0
211	6	4.90	5	1.07927
110_2	8	4.32	8	1.08720
310	10	3.90	6	1.09106
111_2	12	3.52	10	1.08613
321	14	3.20	1	1.07881
100_4	16	3.04	4	1.08493
110_3, 411	18	2.88	2	1.08702
210_2	20	2.72	1	1.08508
332	22	2.58	9	1.08283
211_2	24	2.48	1	1.08445
431, 501	26	2.38	5	1.08406
	28			
521	30	2.22	5	1.08491
110_4	32	2.15	1	1.08501
530	34	2.08	less than 1	1.08380
100_6	36	2.02	less than 1	1.08350
532, 611	38	1.97	3	1.08434
310_3	40	1.92	2	1.08433
541	42	1.87	2	1.08343
311_2	44	1.83	less than 1	1.08417
631	46	missing		
111_4	48	missing		
110_5, 543	50	1.72	8	1.08611
320_2	52	1.68	1	1.08331
100_8	64	1.53	8	1.08492

The weighted mean value for the side of the unit cube is log. a_0 =
1.08493 and a_0 = 12.16 A.U.

A body-centered cube of these dimensions should give two lines not
obtainable when using a General Electric cassette, viz., the line correspond-
ing to the 110 plane (d = 8.61 A.U.), and the 200 (d = 6.08 A.U.).

Their presence was verified by substituting a flat film for the regular
cassette when the following values were obtained.

	Mean	Calculated
M_0-Kα line 14.75 mm. corresponding to d 8.74		
M_0-Kβ line 13.2 mm. corresponding to d 8.65	8.70	8.61
M_0-Kα line 21.0 mm. corresponding to d 6.15		
M_0-Kβ line 19.25 mm. corresponding to d 5.96	6.06	6.08

These values satisfied the theoretically calculated requirements, and
gave 22 consecutive lines, which is considered sufficient to definitely
establish the lattice structure of the acid.

Attempts to obtain the acid in the form of a crystal by dissolving the
acid in anhydrous solvents failed, and it was not possible to get a unit
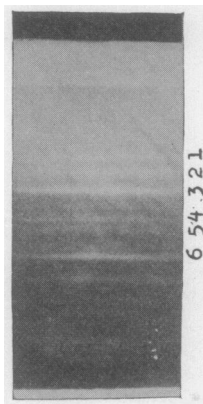large enough to make an examination by the Laue or Bragg methods.

PLATE I.

SPECTROGRAM OF SILICODUODECITUNGSTIC ACID $2H_2O \cdot (6H_2O \cdot SiO_2 \cdot 12WO_3)$.

(Tungsten wire calibration)
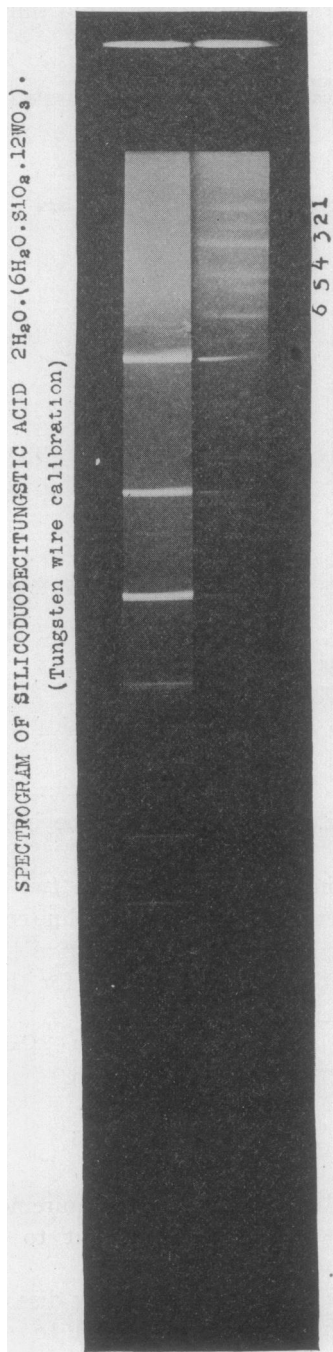
6 5 4 3 2 1

PLATE II.

SPECTROGRAM OF SILICODUODECITUNGSTIC ACID $2H_2O \cdot (6H_2O \cdot SiO_2 \cdot 12WO_3)$.

6 54 321

Six corresponding lines have been marked in each plate.

A body-centered cube may belong to space groups 197 (T^3), 199 (T^5), 204 (T_h^5), 206 (T_d^7), 209 (T_d^3), 212 (T_d^6), 217 (O^5), 220 (O^8), 229 (O_h^9), 230 (O_h^{10}),[6] but of these 206, 212, 220 and 230 require abnormal spacings not present in the lines obtained, and the symmetry requirements of space group 199 cannot be satisfied with only two molecules. The data at hand has not been sufficient to distinguish which of the remaining possibilities 197 (T^3), 204 (T_h^5), 209 (T_d^3), 217 (O^5) and 229 (O_h^9) is the particular group involved.

No spectrograms of the crystals containing 24 or 30 molecules of water of hydration have been obtained, because they effloresce rapidly in air, and do not preserve their crystal structure more than a few minutes, while an exposure of two to three days is necessary to secure a diffraction pattern when using a molybdenum target tube.

The acid when dried in air and containing somewhat more water of crystallization than the acid dried at 100°, and the latter acid containing six molecules of water of crystallization, gave the same spacings as listed in the table above. This was true also of silicodecitungstic acid and silicooctatungstic acid, which were isolated as mentioned in the previous section. The anhydride, however, gave a pattern of much lower symmetry which has not yet been interpreted.

The gravity of the anhydrous acid, $2H_2O.SiO_2.12WO_3$ calculated, from the volume of the unit cell, i.e., $(12.16 \times 10^{-8})^3$, and assuming two molecules to the cell, is 5.32, and of the acid dried at 100°, $2H_2O.SiO_2.12WO_3.-6H_2O$, or $(4H_2O.SiO_2.12WO_3.4H_2O)$ is 5.52. The value obtained by pycnometric methods corresponding to the latter was 5.6.

Since the heteropoly-acids crystallize in the same system, it would be expected that dried phosphomolybdic acid would also form body-centered cubes. Examination of a sample of phosphodecimolybdic acid verified this assumption, the unit cell in this case being 14.31 A.U. on each side. The same technique for obtaining the large spacings as mentioned under silicotungstic acids was employed with similar success in this case.

2. *The Probable Formula and Structure of Silicotungstic Acid.*—In proposing a modified formula for silicotungstic acid, the following facts were considered: (1) it is very difficult to remove the so-called 4 molecules of water of hydration which are retained in the acid when it is dried at 100°; (2) there is no difference in properties or structure when the acid is dried from $2H_2O.SiO_2.12WO_3.6H_2O$ to $2H_2O.SiO_2.12WO_3$, with the loss of six molecules of water; (3) a change in the structure and in the chemical and physical properties of the acid accompanies the removal of the last two molecules of water; (4) the free acid is tetrabasic; and (5) the modified acids with 10 and 8 tungsten atoms are also tetrabasic. From this evidence it is concluded that the acid has 8 molecules of water of constitution,[7] that two of these are acidic, and that the other six are

non-acidic or alcoholic in nature, a condition found in the class of silicates known as the zeolites. The formula of the acid would be written $2H_2O-(6H_2O.SiO_2.12WO_3)$ or $H_4(H_{12}SiW_{12}O_{46})$ or best $H_4[(SiO_4)(W_{12}O_{30})(OH)_{12}]$.

An approximate three-dimensional conception of the molecule of silico-tungstic acid may be described as follows: a central silicon atom is surrounded with four oxygen atoms to form the group SiO_4. This group forms the core of a shell of tungsten atoms which are disposed in a cube-like form. Each tungsten atom with a positive charge of six is surrounded in space by the required number of hydroxyl groups and oxygen atoms at the corners of octahedra. The four oxygens connected with silicon are shared with four of the tungsten atoms which thus have a different relationship in the structure from the other eight tungsten atoms. Each of the four unique tungsten atoms is connected with two other tungsten atoms by sharing in common an oxygen atom. The four unique tungsten atoms which are most closely related to the SiO_4 group hold the acidic hydroxyl groups which account for the tetrabasicity of the acid. Six of the remaining tungsten atoms hold one oxygen and two hydroxyl groups while sharing two other oxygens with neighboring tungsten octahedra. The final two tungsten atoms hold one oxygen instead of the two hydroxyl groups. This structure then accounts completely for the formula $H_4[(SiO_4)(W_{12}O_{30})(OH)_{12}]$.

A molecular structure of this type satisfies the following requirements indicated by chemical investigations of the acid. The linkages of all the alcoholic hydroxyl groups are the same, and are different from the linkages of the acidic hydroxyl groups. Removal of the alcoholic hydroxyl groups forms the acid $2H_2O.SiO_2.12WO_3$, which is tetrabasic and essentially the same in structure as the acid $2H_2O.(6H_2O.SiO_2.12WO_3)$. The octabasic salts are formed by ionization and neutralization of alcoholic hydroxyl groups. In the presence of excess of alkali the outer tungstens are split off leaving salts which are derivatives of acids with less tungsten atoms, fewer hydroxyl groups, but the same basicity as listed in the previous section, viz.,

$$2H_2O.(6H_2O.SiO_2.12WO_3)$$
$$2H_2O.(5H_2O.SiO_2.10WO_3)$$
$$2H_2O.(4H_2O.SiO_2.8WO_3)$$
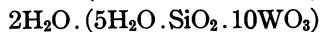
The tungsten atoms are divided into two independent sets of six each which allows the ready substitution of six molybdenum atoms for six tungsten atoms, a fact stressed by Asch and Asch. The change in structure which takes place with the formation of the anhydride can be accounted for by the regrouping of the tungsten and oxygen atoms in the central section following the removal of the acidic hydroxyl groups.

A molecular structure of this type satisfies the requirements indicated

by the x-ray investigation also. Since the unit cube of silicotungstic acid is body centered, and contains two molecules of the acid, it must have one molecule located at the center and one molecule at each corner (each of the eight corner molecules contributes one-eighth to the unit cell), in which case the limiting dimensions of the molecule itself are defined by the value

$$\frac{\sqrt{3} \times 12.16}{2} = 10.53 \text{ A.U.}$$

Goldschmidt[8] gives the diameter of the oxygen ion as 2.62 A.U. and the diameter of the hydrogen ion as 2.54 A.U., while the silicon and tungsten ions are so small that they will fit without appreciable distortion in the hollow formed by four large ions when arranged in one plane. The problem of assigning a structure to silicotungstic is therefore one of placing the large number of oxygen and hydrogen ions in a cubical arrangement, having not more than four of either along a side, since the diameter of the four ions ($4 \times 2.62 = 10.48$ A.U.) is approximately equal to the side of the molecule (10.53 A.U.).

The structure described above has a square cross-section with four large ions to the side and height of somewhat more than four ions, so that it fits the experimentally determined dimensions very closely. Examined from this point of view the long chain structure, the stereo-hexite-pentite structure of Asch and Asch[9] and Rosenheim's coördinated structure are all less satisfactory.

The model of the structure of the molecule just presented must be considered only as a working plan rather than a unique delineation, although it alone accounts satisfactorily for the chemical data and such x-ray results as may be deduced from powder diffraction patterns. Efforts are being continued to the end of preparing single crystals of this acid as well as those for the highly hydrated acid. Only by means of rotation diagrams would it be possible to determine uniquely the parameters involved in a highly complex structure. As to a cubical molecular structure with a central stabilizing SiO_4 group, there can be no question.

Summary.—1. By stepwise addition of alkali to the acid, the amount of alkali necessary to cause the initial decomposition of the acid has been determined, and a series of modified acids with 7, 8 and 10 tungsten atoms has been isolated.

2. X-ray examination of the acid shows that it crystallizes as a body-centered cube, with a side length of 12.16 A.U. This dimension applies to the acids with 8, 10 and 12 tungsten atoms, and to the modifications of the latter that contain two molecules of water ($2H_2O.SiO_2.12WO_3$) or eight molecules of water ($2H_2O.(6H_2O.SiO_2.12WO_3)$) but not to the

anhydride ($SiO_2.12WO_3$). Phosphodecimolybdic acid similarly forms a body-centered cube with a side length of 14.31 A.U.

3. A modified formula for the acid—$2H_2O(6H_2O.SiO_2.12WO_3)$ or $H_4[(SiO_4)(W_{12}O_{30})(OH)_{12}]$—and a new spatial structure have been deduced to correlate adequately the x-ray and chemical data.

[1] Throughout this paper the term silicotungstic acid will be understood to refer to silicoduodecitungstic acid.

[2] This communication is an abstract of a portion of a thesis submitted by Arthur G. Scroggie in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[3] Rosenheim and Jaenicke, *Zeits. anorg. Chem.*, **100**, 319, 1917. Asch and Asch, *The Silicates in Chemistry and Commerce*, Van Nostrand, New York, 1911, p. 95.

[4] See paper No. II of this series, *J. Am. Chem. Soc.* (in press).

[5] Rosenheim and Jaenicke, *Zeits. anorg. Chem.*, **101**, 242, 1918.

[6] Astbury and Yardley, *Phil. Trans. R. Soc. London*, **A224**, 221, 1924.

[7] Asch and Asch, ref. 3.

[8] Glocker, *Materialprüfung mit Röntgenstrahlen*, Springer, Berlin, 1927, p. 274.

[9] Asch and Asch, *The Silicates in Chemistry and Commerce*, Van Nostrand, New York, 1911, p. 281. Rosenheim and Jaenicke, *Zeit. anorg. Chem.*, **100**, 319, 1917.

BINARY SOLUTIONS OF CONSOLUTE LIQUIDS*

By Wilder D. Bancroft and H. L. Davis

Department of Chemistry, Cornell University

It has long been known that the change of the partial pressure with the concentration for ideal solutions can be given accurately over the whole range of concentrations by the so-called Raoult law[1]

$$\frac{N_1}{N_1 + N_2} = \frac{p_2 - p'_2}{p_2}, \qquad\qquad \text{I}$$

where the first term is the mol fraction in the liquid phase and p_2 and p'_2 are the vapor pressure of the pure solvent and the partial pressure of the solvent in the solution, respectively.

We have found empirically that the behavior of other pairs of solutions can be represented with unexpected accuracy by the equation

$$\left(\frac{G_1/M_1}{G_2/M_2}\right)^a = \left(\frac{N_1}{N_2}\right)^a = K\frac{p_2 - p'_2}{p'_2}, \qquad\qquad \text{II}$$

where M_1 and M_2 are the gram-molecular weights of the two components in the vapor, while a and K are empirical constants, which are obtained