

127. *Identification of the 12-Heteropoly-acids and their Salts by Means of X-Ray Powder Photographs.*

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THE structures and formulæ of the heteropoly-acids have long been a subject for speculation, and in the literature there is much confusion, in spite of the fact that these acids are important reagents in biological chemistry and in the dye industry. The present work is concerned

with the 12-acids and their salts. Recently, Keggin (*Proc. Roy. Soc.* 1934, A, **144**, 75) worked out the structure of 12-phosphotungstic acid, finding the formula of the anion to be $(PW_{12}O_{40})^{-3}$, in agreement with the mass of chemical evidence. Signer and Gros (*Helv. Chim. Acta*, 1934, **17**, 1076), working in these laboratories, later showed that the anions of silico-, boro-, and meta-tungstic acids have a similar structure, their formulæ being, therefore, $(SiW_{12}O_{40})^{-4}$, $(BW_{12}O_{40})^{-5}$, and $(H_2W_{12}O_{40})^{-6}$ respectively. Santos (*Proc. Roy. Soc.*, in the press) has shown that the cæsium salts of these acids contain 3 cæsium atoms in the molecule, with 0, 1, 2, or 3 hydrogen atoms, respectively, in addition.

The exceedingly useful X-ray powder method has been used throughout these investigations. The structure of the anion was deduced from a powder photograph of the partially dehydrated phosphotungstic acid, for crystals of this hydrate could not be grown in sufficient size for single-crystal work. This was also the case with many of the salts examined. From similarity of diffraction patterns, we deduce similarity of structure. Furthermore, many of the salts of these acids have a structure closely related to that of the acid. The number and position of the metal ions in the molecule of the potassium, rubidium, cæsium, and thallium salts can be deduced from the differences in intensity of certain lines in the diffraction pattern of the salt and that of the acid. In this manner, numerous salts have been prepared and identified: many were new, but we were unable to confirm the formulæ already assigned to several of the known salts.

The analysis of these complex compounds presents many difficulties, and identification by means of powder photographs is much simpler. The exact determination of the number of molecules of water of crystallisation is a matter of some difficulty owing to the high molecular weight, but this can be deduced from a consideration of the space available when the anions are packed together. A further advantage of the method is that one can judge the purity of the substance under investigation by the presence of absence or stray lines. Also, it is a simple matter to test the stability of the compound to, *e.g.*, heat: any decomposition of the anion would be difficult to detect analytically.

Fig. 1 shows a photograph of the pentahydrate of phosphotungstic acid, and Fig. 2 that of the cæsium salt, taken by Santos: the general patterns are the same in both cases. There is, however, a marked difference in the intensities of certain lines (indicated in Figs. 1 and 2), and from these differences Santos was able to show that the molecule of the salt contained three metal atoms. (The spacings of the salt and the acid are slightly different, but the photographs have been suitably enlarged to facilitate comparison.)

The Structure of 12-Phosphotungstic Acid. (See Keggin, *loc. cit.*)—The large octahedral crystals grown from aqueous solution of this acid gave a very complicated powder photograph. On dehydration over phosphoric oxide in a vacuum for 2 days, 24 molecules of water of crystallisation were lost, and the weight of the acid became constant. This dehydrated form gave a much simpler diffraction pattern (Fig. 1), and from it Keggin deduced the structure and formula of the anion (see Figs. 4 and 5). The twelve tungsten atoms lie, approximately, on the middle of the edges of a cube, at the centre of which lies the phosphorus atom. Four oxygen atoms form a regular tetrahedron around this phosphorus atom, and the remaining 36 oxygens are so arranged that each tungsten atom is surrounded by an octahedron of six oxygens, as shown for one such atom (W_1) in Fig. 4. The O_1 atom is also shared by the octahedra around W_2 and W_3 . There are a number of common edges of the octahedra. The arrangement of the oxygen groups can be seen in Fig. 5, which represents the whole anion.

In the partially dehydrated acid, the packing is cubic, with two molecules per unit cell. The surface of the anion may be considered as consisting of a number of flats (heavily outlined in Fig. 5) and re-entrants. In this packing, the anions are joined flat to flat and re-entrant to re-entrant (see Fig. 6). Of the five molecules of water in this pentahydrate, three are situated at the centres of the faces and the middle of the sides of unit cube, and two between adjoining re-entrants.

Keggin (*Nature*, 1933, **132**, 351) also showed that in the higher hydrate the anions are arranged in a diamond-like packing. There are eight molecules in a unit cell, which has a lattice spacing of 23.28 Å. Recently, Bradley and Illingworth have worked out the position of the molecules of water of crystallisation in this hydrate, and this will be published

FIGS. 1 and 2.

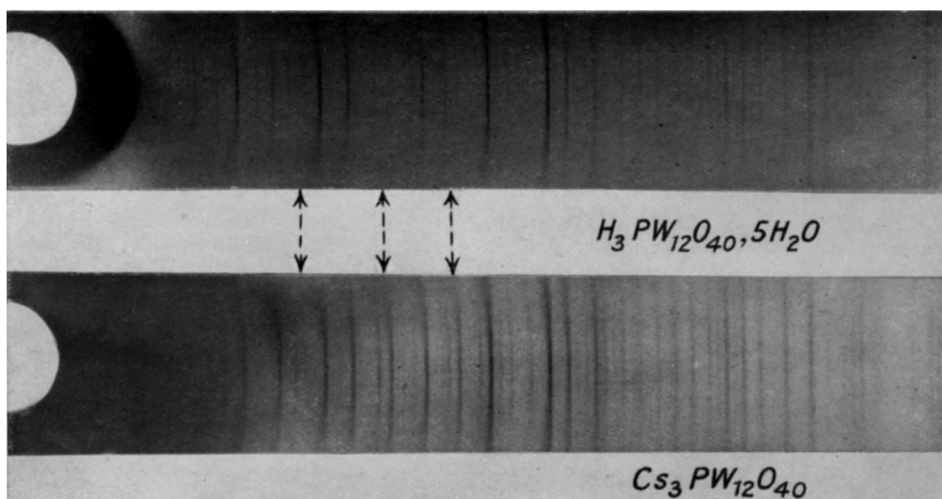
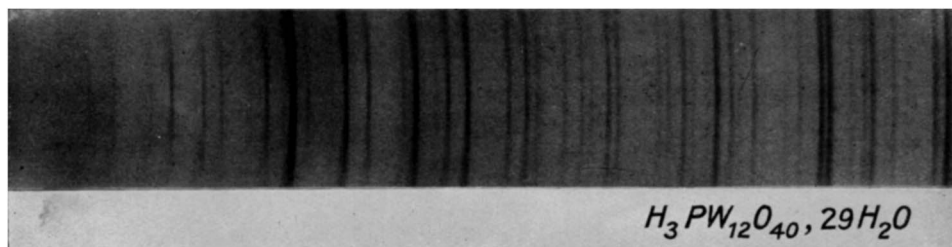
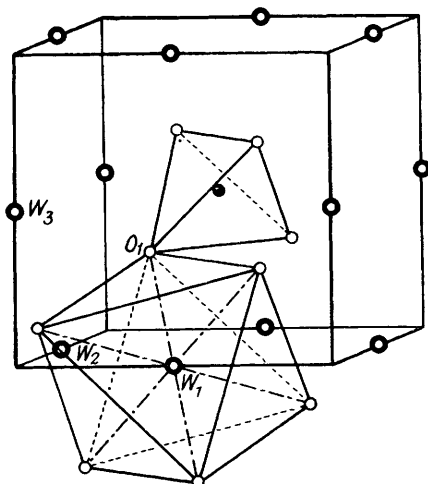


FIG. 3.



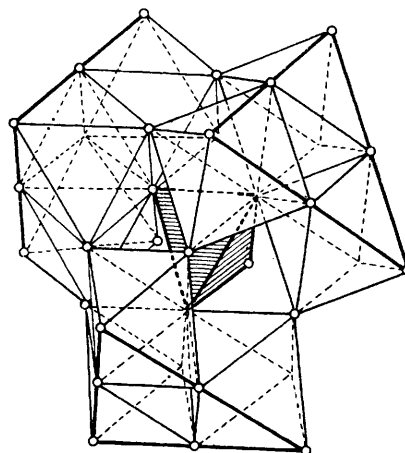
shortly. The anions are joined re-entrant to re-entrant, as shown in Fig. 7. Consideration of this figure shows that there is a large proportion of the cube which is not occupied by the anions, owing to the open nature of the diamond-like arrangement. The water molecules occupy this space, and calculations show that there are 29 H_2O , in agreement with the fact

FIG. 4.



● = Phosphorus atom. ○ = Oxygen atom. ● = Tungsten atom

FIG. 5.



that 24 H_2O are lost in the transition from the higher to the lower hydrate. A section of the powder photograph of this hydrate is shown in Fig. 3.*

Santos (*loc. cit.*) found that caesium phosphotungstate, formed as an insoluble precipitate on addition of a soluble caesium salt to the acid, without dehydration, gave the packing of

FIG. 6.

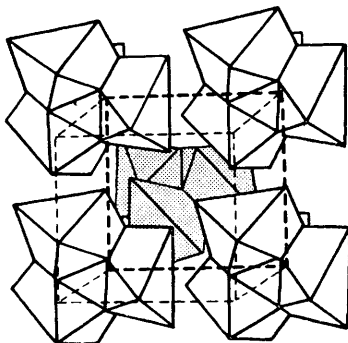
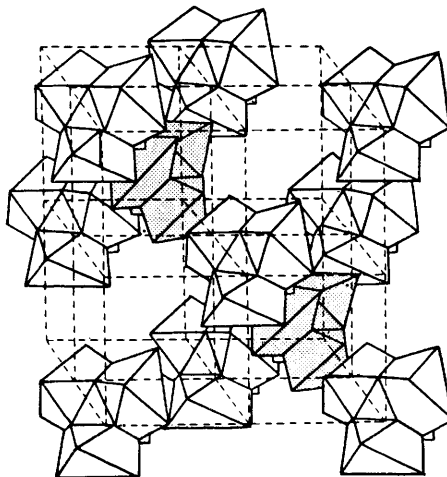


FIG. 7.



the pentahydrate (Fig. 2). He showed that there are three caesium atoms per molecule, and they occupy the positions originally filled by the $3\text{H}_2\text{O}$ at the centres of the faces and the middle of the edges of the unit cube.

The unit cell of those univalent salts which have the pentahydrate packing is smaller

* This photograph was taken in a larger camera than the normal one, and the magnification in Fig. 3 is much greater than in Figs. 1 and 2.

than that of the acid. The size of the anions remains unchanged, but they pack more closely. There is thus less space between the adjoining re-entrants, and in some cases there is not room enough for the molecules of water of crystallisation which occupy this space in the acid state.

EXPERIMENTAL.

The Tribasic 12-Heteropoly-acids and their Univalent Salts.—Phosphotungstic acid. This acid was prepared by Wu's method (*J. Biol. Chem.*, 1920, **43**, 189). It was found that if hydrochloric acid was not added during the last ether extraction, the product was pure 12-phosphotungstic acid, but the omission reduces the yield.

Ammonium phosphotungstate, $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$, is formed as a white, microcrystalline, fairly insoluble precipitate on addition of aqueous ammonium chloride to an acidified solution of the acid.

Sodium phosphotungstate. 50 G. of sodium tungstate dihydrate were dissolved in 100 c.c. of warm water, 5 c.c. of 85% phosphoric acid and 80 c.c. of concentrated hydrochloric acid were added, and the mixture cooled. A white crystalline precipitate of sodium phosphotungstate separated. Its constitution has not been determined, but after being heated for 2 hours at 105° it gave the pentahydrate structure. The formula of this dehydrated form is $\text{Na}_3\text{PW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$, where $n = 2$ or, more probably, 0.

Potassium phosphotungstate, $\text{K}_3\text{PW}_{12}\text{O}_{40}$, is formed as a white microcrystalline powder on addition of a soluble potassium salt to the acid. Unlike the sodium salt, it is fairly insoluble, and no dehydration is necessary to give the pentahydrate structure.

In a similar manner, rubidium, caesium and thallium phosphotungstates, $\text{M}_3\text{PW}_{12}\text{O}_{40}$, were all precipitated with pentahydrate packing.

Phosphomolybdic acid. This acid was prepared by Wu's method (*loc. cit.*). The yellow octahedra which crystallise from aqueous solution give a powder photograph similar to Fig. 3. The formula is, therefore, $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 29\text{H}_2\text{O}$. Attempts to prepare a pentahydrate cubic packing of this acid were unsuccessful. On dehydration, the colour of the acid changed to green, indicating decomposition of the molecule. It is probable that the acid is unstable to the dehydrating conditions necessary to produce the lower hydrate.

On the other hand, the ammonium, sodium, potassium, rubidium, caesium, and thallium salts all gave the 5-hydrate packing; except the sodium salt, all are very insoluble. The acid will detect 1 part of potassium or caesium in 10,000 or 500,000 parts of solution, respectively (Illingworth and Santos, *Nature*, 1934, **134**, 971).

Ammonium phosphomolybdate, $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$, was prepared by adding an aqueous solution of ammonium chloride to an acidified solution of the acid. The canary-yellow precipitate had the usual pentahydrate packing.

Sodium phosphomolybdate is soluble, and can be prepared by addition of sodium chloride solution to the acid. The crystals obtained gave an unknown packing, but on drying for 2 hours at 105°, the normal pentahydrate packing was obtained. The formula of this dehydrated form is $\text{Na}_3\text{PMo}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$, where $n = 2$ or 0.

The potassium salt, $\text{K}_3\text{PMo}_{12}\text{O}_{40}$, was similarly prepared; the canary-yellow precipitate showed the usual packing. This compound is very stable, and powder photographs show that its constitution is unchanged after heating for several hours at 120°. The yellow rubidium, caesium, and thallium salts are prepared in the same manner and have analogous formulæ.

Arsenotungstic acid. No 12-acid is reported in the literature, and all attempts to prepare it were unsuccessful.

Ammonium arsenotungstate is the only salt of the 12-acid previously reported. It is prepared by adding concentrated ammonium chloride solution to a mixture of sodium tungstate and sodium arsenate solutions, strongly acidified with hydrochloric acid. On boiling, a white precipitate, $(\text{NH}_4)_3\text{AsW}_{12}\text{O}_{40}$, is formed. Powder photographs show the normal 5-hydrate packing.

A similar procedure afforded the potassium and the rubidium salt, $\text{M}_3\text{AsW}_{12}\text{O}_{40}$, which are insoluble and have the usual 5-hydrate structure. Attempts to prepare a caesium salt with a similar packing were unsuccessful.

Arsenomolybdic acid. Here again, no 12-acid is reported, and it could not be prepared.

The ammonium salt, $(\text{NH}_4)_3\text{AsMo}_{12}\text{O}_{40}$, is formed as a canary-yellow precipitate on boiling a mixture of sodium arsenate, sodium molybdate, nitric acid, and ammonium chloride; it has the normal 5-hydrate packing.

The potassium and the rubidium salt were prepared by adding the corresponding chloride to

a boiling mixture of sodium arsenate and sodium molybdate solutions and hydrochloric acid. The canary-yellow precipitates, of formula $M_3AsMo_{12}O_{40}$, are very insoluble.

The Tetrabasic Acids.—Silicomolybdic acid was prepared in a similar manner to the corresponding phosphomolybdic acid, sodium silicate solution being used instead of phosphoric acid. In this case, the ether extraction of the acid is more difficult, and care must be taken to avoid excess of hydrochloric acid, otherwise the ether compound will not form. On standing, the aqueous solution becomes yellowish-green, and hexagonal crystals are formed; these were of unknown packing. If, however, a few drops of nitric acid were added to the acid solution, and crystallisation was effected above 30° , small yellow octahedral crystals were formed. These gave a powder photograph similar to Fig. 3, and their formula is, therefore, $H_4SiMo_{12}O_{40}\cdot 29H_2O$.

Attempts to prepare the 5-hydrate packing were unsuccessful. The acid, on dehydration, rapidly became green—an indication that the anion was disintegrating.

Ammonium silicomolybdate. Parmentier (*Compt. rend.*, 1887, 92, 1234) reported the precipitation of a salt, $(NH_4)_4H_4Si(Mo_2O_7)_6\cdot nH_2O$, on mixing nitric acid solutions of ammonium molybdate and alkali silicate. If we assume that the basicity of the acid is not eight but four, then, according to Parmentier, this is a normal salt.

The authors prepared the salt by adding excess ammonium chloride solution to the acid; the canary-yellow precipitate had the 5-hydrate packing. Owing to the comparatively low scattering power of the ammonium ion, it is impossible to deduce from the powder photograph the number of these ions in the molecule. However, symmetry conditions of the structure do not allow of a four position in the 5-hydrate packing, and we concluded that this must be an acid salt, as in the case of caesium silicotungstate (Santos). Subsequently, chemical analysis proved conclusively that the ammonium content was 3 and not 4; the formula is, therefore, $(NH_4)_3HSiMo_{12}O_{40}$. Attempts to prepare the normal salt were unsuccessful.

The potassium salt was prepared by adding excess potassium chloride solution to the acid; unlike the corresponding phosphomolybdate, it is soluble. If the solution is allowed to crystallise, yellow hexagonal prisms are obtained. These gave an unknown packing, but on heating for 2 hrs. at 120° , the normal cubic packing was obtained. The formula of this dehydrated form is $K_3HSiMo_{12}O_{40}$.

Analogous formulæ are possessed by the rubidium, caesium, and thallous salts, prepared by adding a solution of a salt of the appropriate metal to the acid; they are all insoluble and give the usual 5-hydrate packing.

Silicotungstic acid. Signer and Gros (*loc. cit.*) showed that the dehydrated form of this acid gave a similar packing to that of phosphotungstic acid, and the formula was therefore $H_4SiW_{12}O_{40}\cdot 5H_2O$. The higher hydrate, however, was not cubic but hexagonal, and had a similar packing to the hexagonal form of silicomolybdic acid; it lost $24H_2O$ on transition to the 5-hydrate, and is therefore $H_4SiW_{12}O_{40}\cdot 29H_2O$.

The potassium salt, prepared by adding excess potassium chloride solution to the acid, is soluble. According to various workers, it is the normal salt, but on dehydration it did not give the normal 5-hydrate packing. It is significant that, if the 4-salt is formed, then the packing is no longer that of the 5-hydrate. This is, of course, in agreement with theory.

The thallous salt, $Tl_3HSiW_{12}O_{40}$, is formed as a white precipitate on addition of a solution of a soluble thallous salt to the acid.

The 12-Manganimolybdates.—These salts have not hitherto been described. Attempts to prepare the free acid were unsuccessful.

Ammonium manganimolybdate. 5 G. of sodium molybdate were dissolved in 10 c.c. of water, and 0.5 g. of sodium permanganate added. The mixture was heated, 10 c.c. of hydrochloric acid added, and boiling on the water-bath continued for an hour, the solution becoming deep yellow. The mixture was filtered and excess of concentrated ammonium chloride solution added to the filtrate. On boiling, a pale yellow precipitate formed, having the normal 5-hydrate packing. This salt is derived from the acid $H_nMnMo_{12}O_{40}$, and since manganese may be either quadri- or septa-valent, $n = 4$ or 1. The value of n would be very difficult to obtain by ordinary chemical analysis and no attempt has yet been made to do so. All attempts to prepare a 12-heteropoly-acid with a charge of $+6$ at the centre have been unsuccessful, and we are led to assume that such a charge would render the whole anion unstable. If so, then it appears improbable that a charge of $+7$ can be placed in the centre, and $n = 4$; in agreement with this, the salt has a spacing identical with that of ammonium silicomolybdate (11.63 Å). Analysis indicated 3 ammonium ions per molecule. The formula is, therefore, $(NH_4)_3HMnMo_{12}O_{40}$.

The caesium salt was similarly prepared by use of caesium sulphate; the pale yellow precipitate had the 5-hydrate packing.

Germanitungstic Acid.—We are indebted to Mr. W. O'Leary, of Cornell University, for kindly sending us a sample of this acid. Its preparation is described by Brukl (*Monatsh.*, 1930, 59, 179) and Schwartz and Giese (*Ber.*, 1930, 63, 2428). No cubic form of the 29-hydrate could be obtained, but after dehydration over phosphoric oxide in a vacuum for 4 days, the weight became constant and the normal 5-hydrate packing was obtained. The formula is thus $H_4GeW_{12}O_{40}, 5H_2O$.

The white caesium salt, $Cs_3HGeW_{12}O_{40}$, is precipitated on addition of a soluble caesium salt to a solution of the acid.

Ammonium Titanimolybdate, $(NH_4)_3HTiMo_{12}O_{40}$.—0.3 G. of titania was fused with excess of acid potassium fluoride on a carbon block, and the resulting white mass added to a solution of 5 g. of sodium molybdate in 10 c.c. of water; 15 c.c. of concentrated hydrochloric acid and a few drops of nitric acid were added, and the whole heated on the water-bath for an hour. The mixture was then filtered, and the filtrate treated with excess of concentrated ammonium chloride solution and boiled; the golden-yellow precipitate had the simple cubic 5-hydrate structure. Great care must be taken in this preparation to avoid contamination with silica, for ammonium silicomolybdate is then formed.

Ammonium zirconimolybdate is prepared in an analogous manner and gives an identical powder photograph.

Borotungstic Acid.—Signer and Gros (*loc. cit.*) showed that this acid has a structure similar to that of $H_3PW_{12}O_{40}$. No cubic form of the 29-hydrate could be grown, but on dehydration of this higher hydrate over phosphoric oxide in a vacuum for 8 days, $H_5BW_{12}O_{40}, 5H_2O$ was obtained.

Metatungstic Acid.—This belongs to the series of 12-acids. No cubic form of the higher hydrate could be obtained, but dehydration as above for 4 hours afforded $H_6(H_2W_{12}O_{40}), 5H_2O$.

The caesium and the thallos salt, $M_3H_3(H_2W_{12}O_{40})$, are precipitated on addition of a soluble salt of the metal to the acid; the former is fairly soluble in hot water.

Attempts to prepare 12-Acids.—Although metatungstic acid is a 12-heteropoly-acid, all attempts to prepare an analogous metamolybdic acid or its salts failed. No 12-boromolybdates are known, and they could not be prepared. As metamolybdic and 12-boromolybdic acids probably do not exist, we infer that a charge of + 5 or + 6 at the centre of the anion renders the latter unstable in the case of the complex 12-molybdic acids. In the corresponding tungstic acids, the stability of the anion diminishes with increasing charge.

Attempts to prepare 12-stanni-, chromo-, antimo-, and vanado-molybdates were all unsuccessful. Although efforts were made with many elements (*e.g.*, Al and Cr), it was found possible to place only molybdenum and tungsten in the outer shell of the 12-acid.

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