

## Dodecatungstophosphoric Acid Hexahydrate, $(\text{H}_5\text{O}_2^+)_3(\text{PW}_{12}\text{O}_{40}^{3-})$ . The True Structure of Keggin's 'Pentahydrate' from Single-Crystal X-ray and Neutron Diffraction Data\*

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The structure of Keggin's [*Proc. Roy. Soc.* (1934), A144, 75–100] dodecatungstophosphoric acid 'pentahydrate' was redetermined with extensive X-ray and neutron diffraction data from single crystals. The 'pentahydrate' is really the hexahydrate of formula  $(\text{H}_5\text{O}_2^+)_3(\text{PW}_{12}\text{O}_{40}^{3-})$ . The six water molecules are paired in nearly planar diaquahydrogen ions  $\text{H}_5\text{O}_2^+$  (symmetry 222), which have linear centred  $\text{O} \cdots \text{H} \cdots \text{O}$  bonds only 2.370 (5) Å long (2.414 Å corrected for thermal motion), each such ion being in twofold disorder on a  $\bar{4}2m$  site. The  $\text{H}_2\text{O}$  valence angle is 118.7 (5)°. An alternative interpretation consistent with the thermal parameters is that the  $\text{H}_2\text{O} \cdots \text{H}$  of each end of the  $\text{H}_5\text{O}_2^+$  ion has the geometry of a rather flat pyramid and that additional disorder of the O atoms about the twofold axis on which they appear to lie produces apparent 222 symmetry for the  $\text{H}_5\text{O}_2^+$  ion. The structure of the anion  $\text{PW}_{12}\text{O}_{40}^{3-}$  ( $\bar{4}3m$  symmetry) is essentially that of Keggin, though the O atoms are shifted 0.17 to 0.25 Å from the positions Keggin gave. The structure will readily accommodate the extra acidic H atoms of the isomorphous hexahydrates (so-called 'pentahydrates') of silico-, boro- and metadodecatungstic acids. It is inferred that the various structurally similar salts of univalent cations with 12-heteropoly anions, such as  $\text{Cs}_3(\text{PW}_{12}\text{O}_{40})$ , in which the cations are at the  $\bar{4}2m$  sites replacing  $\text{H}_5\text{O}_2^+$  ions, are all properly to be formulated as anhydrous salts. Crystal data: cubic  $Pn\bar{3}m$ .  $a = 12.506$  (5) Å [ $23.5 \pm 1$  °C,  $\lambda(\text{Mo } K\alpha_1) = 0.70926$  Å],  $Z = 2$ ,  $d_c = 5.53$ ,  $d_o = 5.60$  g cm<sup>-3</sup> (Keggin, 1934),  $V_{\text{cell}} = 1793.9$  Å<sup>3</sup>, formula weight 2989.1.

### Introduction

Knowledge of the atomic configuration of the anion  $\text{PW}_{12}\text{O}_{40}^{3-}$  of dodecatungstophosphoric acid (12-phosphotungstic acid) is of central importance in relation to the structures of heteropoly acids. The anion and analogs of it with other atoms replacing either P or W or both are known to occur in at least 80 crystalline compounds (Evans, 1971). When this work was started, the structure of the anion was known only roughly as inferred from X-ray powder diffraction data on dodecatungstophosphoric acid 'pentahydrate' (Keggin, 1934) and on the 29-hydrate (Bradley & Illingworth, 1936). Our reinvestigation‡ by X-ray and neutron single-crystal diffraction methods shows that the 'pentahydrate' is actually the *hexahydrate* with formula  $(\text{H}_5\text{O}_2^+)_3(\text{PW}_{12}\text{O}_{40}^{3-})$ , in which the anion structure is essentially that described by Keggin. Allmann & d'Amour (1974, 1975) have determined the structure of the same anion in triclinic  $\text{NaH}_2(\text{PW}_{12}\text{O}_{40}) \cdot x\text{H}_2\text{O}$  ( $x = 12-14$ ).

### Data

Single crystals were grown from concentrated nitric acid solutions at about 90 °C. The crystal used in the neutron work was grown at 90 °C by diffusion of nitric acid from a concentrated solution into an aqueous solution of dodecatungstophosphoric acid. X-ray powder and precession photographs established the identity of the material with Keggin's (1934) 'pentahydrate'. The space group  $Pn\bar{3}m$  ( $O_h^h$ ) was confirmed by noting for both X-rays and neutrons the systematic absences  $0kl$  for  $k + l = 2n + 1$  (C) and no others and by identifying the Laue symmetry as  $m\bar{3}m$ . The cell translation  $a = 12.506$ (5) Å was established by the least-squares method from angle data recorded at  $23.5 \pm 1$  °C for nine resolved  $\text{Mo } K\alpha_1$  reflections ( $\lambda = 0.70926$  Å) between 48 and 49°  $2\theta$ .

The first stage of the structure refinement was carried out with  $F_o^2$  values derived from 3373  $\text{Mo } K\alpha$  intensity data [one octant of reciprocal space to  $(\sin\theta)/\lambda = 0.705$  Å<sup>-1</sup>, including some duplications, representing 528 symmetry-independent reflections] recorded with the Oak Ridge computer-controlled diffractometer (Busing, Ellison, Levy, King & Roseberry, 1968). From its dimensions, the crystal was estimated to weigh  $\sim 5 \times 10^{-6}$  g. The recording technique, which involved both  $\omega$  and  $2\theta$  scans, and the preliminary data processing were essentially as described by Hall & Brown (1971). Absorption correc-

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‡ Preliminary reports of this work were given earlier (Noe-Spirlet, Brown, Busing & Levy, 1974, 1975).

tion factors calculated by the Busing & Levy (1957) method were applied ( $\mu = 407 \text{ cm}^{-1}$ , minimum correction factor for  $F_o^2 = 8.72$ , maximum = 31.6). Anisotropic extinction corrections of type 1 (Coppens & Hamilton, 1970) were applied near the end of refinement with the X-ray data, before the averaging of the equivalent reflections, to obtain the set of 528 independent  $F_o^2$ 's used in the last least-squares cycles. The maximum correction factor was 1.98. After averaging, the variances of the  $F_o^2$  data were corrected empirically by the addition of the term  $(0.02 F_o^2)^2$  (Peterson & Levy, 1957). Of the 528 average data, 440 had  $F_o^2$  values greater than  $\sigma$ .

The second, more definitive stage of refinement was done with  $F_o^2$  data derived from 2975 neutron intensities [one octant of reciprocal space to  $(\sin \theta)/\lambda = 0.727 \text{ \AA}^{-1}$  plus the  $hhh$  reflections of all other octants, representing 575 independent reflections] recorded with the computer-controlled diffractometer at the High-Flux Isotope Reactor. The neutron wavelength was 1.246 Å. The crystal specimen weighed 98 mg. Absorption corrections (minimum = 1.241, maximum = 1.369,  $\mu = 1.10 \text{ cm}^{-1}$ ), anisotropic extinction corrections (maximum = 3.24), and a variance correction  $(0.03 F_o^2)^2$  were applied, as in the X-ray analysis. Of the 575 average  $F_o^2$  data, 534 had values greater than  $\sigma$ .

### Refinement

#### X-ray

In the first stage of refinement with the X-ray data, by standard Fourier, difference-map, and least-squares

methods, the general correctness of the Keggin approximation to the structure of the anion  $\text{PW}_{12}\text{O}_{40}^{3-}$  ( $\bar{4}3m$  symmetry) was confirmed, but the Keggin water O atoms were found to be incorrect in number and incorrectly positioned. Keggin placed six water O atoms in the cell at the positions  $6-d-42m^*$  (coordinates  $\frac{1}{4}, \frac{3}{4}, \frac{3}{4}$ ;  $\frac{3}{4}, \frac{1}{4}, \frac{3}{4}$ ; etc.) (*International Tables for X-ray Crystallography*, 1952) and four water O atoms at the positions  $4-c-3m$  ( $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ;  $\frac{1}{2}, 0, 0$ ; etc.), whereas we find 24 'half' O atoms, designated O(W), in positions  $24-h-2$  ( $x, \frac{1}{4}, \frac{3}{4}$ ;  $\bar{x}, \frac{1}{4}, \frac{3}{4}$ ; etc.). The compound is therefore the hexahydrate rather than the pentahydrate.

The H atoms could not be found from an X-ray difference map, but they were included in the final least-squares cycles in fixed positions corresponding to a sensible hydrogen-bonding scheme (described below) and to the known geometry of the water molecule. The 48 'half' H atoms H(W) belonging to the water molecules were placed in general positions, and the acidic protons H(A) were assumed to be at the positions  $6-d-42m$ , where Keggin had placed O atoms. The final measures of goodness of fit based† on all 528 independent X-ray reflections are as follows:  $R(F) = 0.059$ ;  $R(F^2) = 0.050$ ;  $R_w(F^2) = 0.065$ ;  $\sigma_1 = 1.29$  (the standard deviation of an observation of unit weight). The least-squares refinement used the  $F_o^2$  values as observational data. The scattering factors used were as follows: O

\* Abbreviation for 6 positions, Wyckoff notation  $d$ , point symmetry  $\bar{4}3m$ . Throughout this paper, coordinates are referred to an origin at  $\bar{3}m$ .

† These measures have been defined explicitly by Hall & Brown (1971) and in many other places.

Table 1. Fractional coordinates ( $\times 10^5$ ) and thermal parameters ( $\times 10^4$ ), for  $(\text{H}_5\text{O}_2^+)_3(\text{PW}_{12}\text{O}_{40}^{3-})$  from X-ray refinement (rows marked X) and from neutron refinement (rows marked N)

The  $U_{ij}$ 's are the parameters of the anisotropic temperature factor  $\exp[-2\pi^2 a^* (h^2 U_{11} + k^2 U_{22} + l^2 U_{33} + 2hkU_{12} + 2hlU_{13} + 2klU_{23})]$ . The standard errors given in parentheses correspond to the least significant digits of the parameters. Parameters unaccompanied by standard errors are either fixed by symmetry or related to others of the same atom by symmetry, except the X-ray coordinates for H(W) and X-ray  $U_{ij}$  parameters for H(W) and H(A), none of which were adjusted. The fractional occupancy is  $\frac{1}{2}$  for O(W) and H(W) and one for all other atoms.

		x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
P	X	75000	75000	75000	137 (19)	137	137	0	0	0
	N	75000	75000	75000	115 (4)	115	115	0	0	0
W	X	75821 (4)	95680 (3)	95680	200 (3)	170 (2)	170	0 (2)	0	-58 (2)
	N	75822 (7)	95688 (4)	95688	207 (3)	173 (2)	173	-2 (2)	-2	-58 (3)
O(1)	X	82252 (69)	82252	82252	180 (31)	180	180	-13 (35)	-13	-13
	N	82273 (5)	82273	82273	155 (2)	155	155	-10 (2)	-10	-10
O(2)	X	65617 (47)	84383	99326 (67)	163 (26)	163	192 (45)	-60 (34)	3 (25)	-3
	N	65683 (4)	84317	99316 (6)	228 (2)	228	189 (3)	-23 (2)	9 (2)	-9
O(3)	X	87223 (48)	87223	102398 (68)	199 (27)	199	175 (45)	47 (35)	-87 (27)	-87
	N	87155 (4)	87155	102447 (6)	249 (2)	249	178 (3)	4 (2)	-36 (2)	-36
O(4)	X	73311 (65)	105452 (51)	105452	327 (56)	315 (33)	315	-15 (29)	-15	-158 (44)
	N	73276 (8)	105441 (5)	105441	375 (4)	285 (2)	285	13 (2)	13	-149 (3)
O(W)	X	75000	115472 (190)	125000	1200 (257)	552 (146)	371 (134)	0	-124 (121)	0
	N	75000	115248 (19)	125000	844 (17)	337 (9)	232 (9)	0	-8 (9)	0
H(W)	X	74503	110148	119100	708	708	708	0	0	0
	N	74525 (24)	111259 (25)	118288 (23)	678 (17)	511 (15)	385 (11)	14 (11)	10 (10)	-81 (11)
H(A)	X	75000	125000	125000	552	552	552	0	0	0
	N	75000	125000	125000	449 (18)	442 (11)	442	0	0	0

and P from *International Tables* (1962); W from Cromer & Waber (1965); H from Stewart, Davidson & Simpson (1965). Anomalous scattering factors  $\Delta f'$  and  $\Delta f''$  from Cromer & Liberman (1970) were used for P and W. Coordinates and thermal parameters are given in Table 1\*.

### Neutron

In the second stage of least-squares refinement, in which the neutron data were used, the coordinate changes were slight. Even for the half H atom of the water molecule the shift from the position assumed in the X-ray analysis was only  $\sim 0.1$  Å. In the penultimate refinement with all 575 averaged  $F_o^2$  data, corrected for extinction, the occupancy factor of the water molecule was found to be 0.506 (6), only one standard deviation greater than the maximum value of 0.5, above which there would have to be simultaneous occupancy of adjacent  $24-h-2$  sites only  $\sim 1.7$  Å apart. With the occupancy factor held fixed at 0.5, refinement converged with the following measures of goodness of fit:  $R(F) = 0.046$ ;  $R(F^2) = 0.041$ ;  $R_w(F^2) = 0.125$ ;  $\sigma_1 = 2.35$ .

The somewhat unsatisfactory values of  $R_w(F^2)$  and  $\sigma_1$  were easily seen to be related to an unusual number of large positive quantities  $(F_o^2 - F_c^2)/\sigma(F_o^2)$ , as large as 20.7, associated with reflections having two odd indices and one even index and having generally small, or at most moderately large,  $F_o^2$  values. The histograms made during recording of the intensity data for these reflections show no abnormalities. There is good agreement among the individual  $F_o^2$  values for the equivalent reflection from which the averages were derived. The latter fact makes it highly improbable that multiple reflection was the cause of the discrepancies, since the crystal was not mounted so that any equivalent reflections could be affected by multiple reflection in the same way, except by accident. It appears that there is some minor fault in our model for the structure.

A difference map calculated at this stage shows maximum excursions of density of  $\sim 10$  times the usual magnitude at the same stage in other neutron refinements in this laboratory, but consideration of the positions of the maxima and minima in the map has not led to any improvement of the model. The largest positive excursion of density corresponds approximately in position to that of atom O(1) inverted through the P atom, suggesting disorder involving two anions related by inversion. However, there are no corresponding peaks for the other atoms of the anion, and this excursion

is only 0.038 times the height of atom O(1) in the Fourier map. Modifying the model by allowing for disorder of the central tetrahedron of O(1) atoms did not improve the fit. The deepest hole in the difference map, 0.059 times the depth of atom H(4), has no obvious interpretation.

We made an attempt, without success, to find an explanation for the discrepancies between  $F_o$  and  $F_c$  in an ordered arrangement of the diaquahydrogen ions. An ordered arrangement implies either an enlarged unit cell or a cell of reduced symmetry. The first possibility was tested by carrying out  $2\theta$  scans of several central lattice rows in an unsuccessful search for superlattice reflections. To assess the second possibility, we considered an ordered arrangement having the same cell dimensions and the symmetry of space group  $P4_232$  and another having the symmetry of  $Pn3$ . The former lacks the inversion centers and does not require the systematic absence of reflections  $Ok\bar{l}$  with  $k+l$  odd ( $\odot$ ). The latter implies reduced Laue symmetry ( $hkl \neq khl$ ) and crystal twinning to conform to the observed symmetry of the diffraction data. Structure factors computed for both types of ordering are in gross disagreement with observation. We conclude that the explanation of the discrepancies does not involve ordering of the  $\text{H}_5\text{O}_2^+$  ions in any simple manner. Also tested and ruled out was the possibility that the crystal was twinned, with a minor component having the symmetry of space group  $I43m$ . For this space group, which was considered and rejected by Keggin (1934), the two anions per cell are related only by the body centering, whereas for  $Pn3m$  they are related by inversion.

Having had no success in improving the model, we decided to omit in final least-squares cycles all reflections for which  $|F_o^2 - F_c^2|/\sigma(F_o^2) > 3$ . By this criterion we omitted 29 reflections with two odd indices and one even index and 5 other reflections. The measures of goodness of fit were:  $R(F) = 0.035$ ;  $R(F^2) = 0.031$ ;  $R_w(F^2) = 0.061$ ;  $\sigma_1 = 1.142$ . The average magnitude of the excursions of electron density in the difference map subsequently computed omitting the 34 discrepant reflections was about half that of the previous map. The standard errors of the atomic parameters were reduced by about a factor of two, but the parameter shifts were of no chemical significance.

The propriety of excluding the discrepant data in final refinement is a legitimate question for debate. We argue that the best parameter determination that can be made based on our model, the most satisfactory one we have been able to devise, will be obtained when those data which clearly do not fit the model are omitted. This point of view seems to be consistent with that of Tukey (1974), who suggests drastically reducing the weights of the outlier observations in least-squares refinements. Nevertheless, one may not wish to take at face value the standard errors derived when the discrepant data are omitted.

\* A list of X-ray and neutron structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32156 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

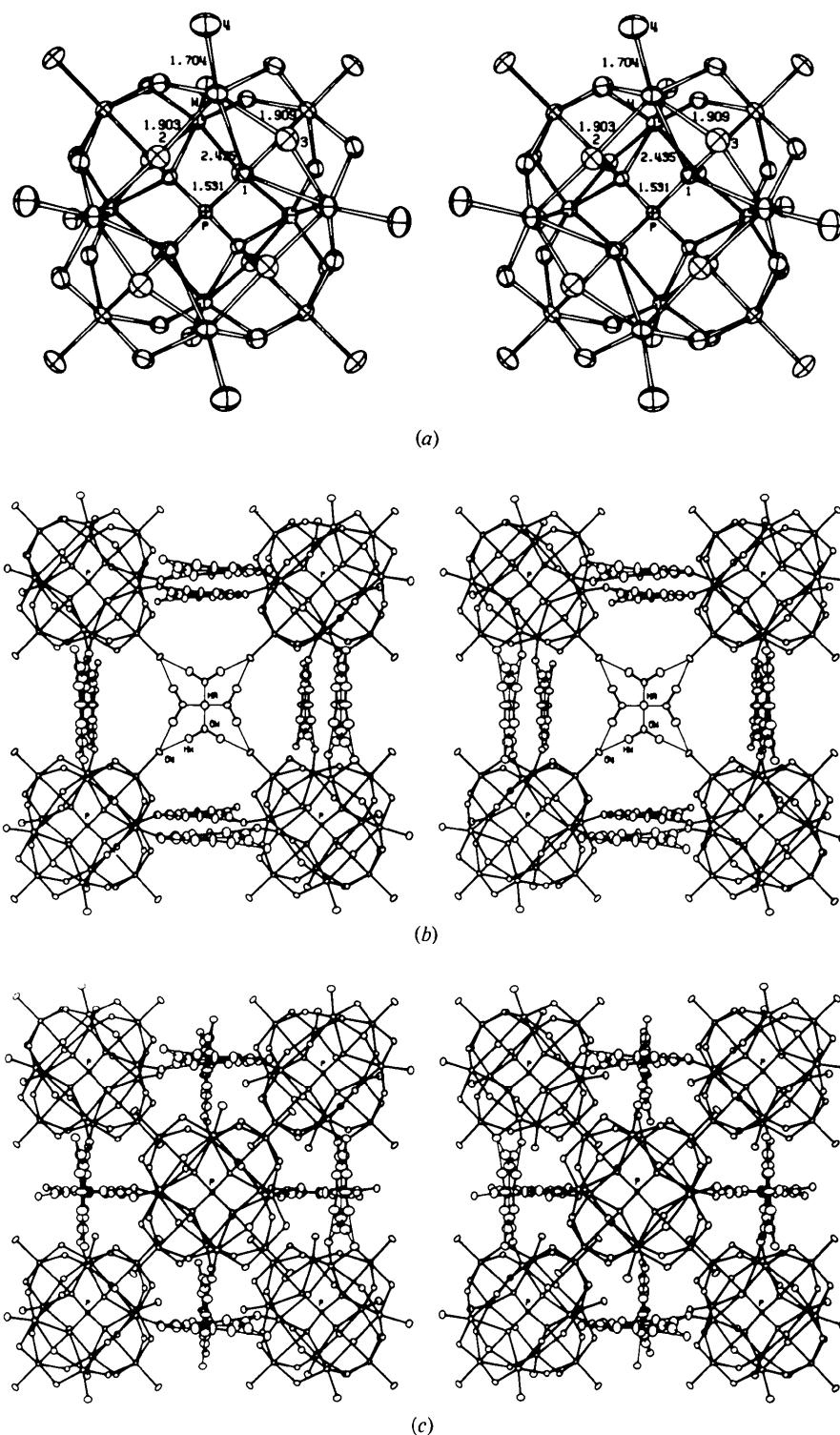


Fig. 1. (a) Stereoscopic view of the  $(PW_{12}O_{40})^{3-}$  anion in the 12-phosphotungstic acid hexahydrate crystal, showing the thermal ellipsoids of 50% probability. View direction is along  $-c$ ; a is along the horizontal from left to right. The atoms of the asymmetric unit are labeled, the numbers 1 through 4 indicating atoms O(1) through O(4). Bond lengths ( $\text{\AA}$ ) are shown. (b), (c) Stereoscopic drawings showing the packing of anions and diaquahydrogen ions. The ellipsoids of 20% probability are shown. Orientation is the same as in (a). Representative atoms O(W), H(W), and H(A) are labeled OW, HW, HA. See text for explanation. Drawings were made with *ORTEP* (Johnson, 1976).

Three other cycles of refinement were calculated omitting 77 reflections which had  $F_c^2$  values so small as to suggest that their phases were not reliably determined. Since no significant parameter changes occurred and only one structure factor changed sign, the results of these cycles are not reported here.

The coordinates and thermal parameters from the neutron refinement are given in Table 1.\* The neutron scattering lengths used were:  $b_p = 0.511$ ,  $b_w = 0.477$ ,  $b_o = 0.5804$ ,  $b_H = -0.3739$ , all in units of  $10^{-12}$  cm. These are almost identical with values given by Shull (1972).

## Discussion

### The anion $\text{PW}_{12}\text{O}_{40}^{3-}$

The structure of the anion  $\text{PW}_{12}\text{O}_{40}^{3-}$  is shown stereoscopically in Fig. 1(a). Interatomic distances and angles within the anion as determined in the neutron refinement are given in Table 2, with standard errors computed from the least-squares covariance matrix. The corresponding distances and angles from the X-ray refinement are not included because they are not significantly different. Comparison of our atomic parameters and bond lengths for the anion with those of the anion as determined by Keggin (1934), Bradley & Illingworth (1936), and Allmann & d'Amour (1975) have been made by the latter authors,† who reported

\* See footnote on p. 1040 concerning tables deposited.

† Allmann & d'Amour (1975) and d'Amour & Allmann (1976) quote distances in our anion which are based on our final X-ray parameters. The coordinates in ångströms which they quote from our work correspond to our penultimate neutron parameters.

Table 2. Distances and angles within the  $(\text{PW}_{12}\text{O}_{40}^{3-})$  anion, with standard errors

P—O(1)	1.5305 (11) Å	O(1)—P—(1 <sup>i</sup> )	109.47°
W—O(1)	2.4349 (10)	P—O(1)—W	125.96 (3)
W—O(2)	1.9029 (6)	P—O(1)—O(2)	93.46 (2)
W—O(3)	1.9094 (7)	P—O(1)—O(3)	144.16 (2)
W—O(4)	1.7041 (11)	O(1)—W—O(2)	82.96 (4)
O(1)···O(1 <sup>i</sup> )	2.4993 (17)	O(1)—W—O(3)	72.08 (3)
O(1)···O(2)	2.9006 (6)	O(2)—W—O(3)	88.45 (3)
O(1)···O(3)	2.5909 (11)	O(2)—W—O(2 <sup>ii</sup> )	85.26 (6)
O(2)···O(2 <sup>ii</sup> )	2.5774 (13)	O(2)—W—O(3 <sup>iii</sup> )	154.82 (5)
O(2)···O(3)	2.6590 (8)	O(2)—W—O(4)	103.08 (4)
O(2)···O(4)	2.8271 (8)	O(3)—W—O(3 <sup>iii</sup> )	86.96 (6)
O(3)···O(3 <sup>iii</sup> )	2.6278 (13)	O(3)—W—O(4)	102.09 (4)
O(3)···O(4)	2.8130 (8)	W—O(2)—W <sup>v</sup>	152.43 (5)
		W—O(3)—W <sup>v</sup>	126.75 (6)

### Symmetry transformations

- |                            |                            |
|----------------------------|----------------------------|
| (i) $x, 1.5 - y, 1.5 - z$  | (iv) $1.5 - z, 1.5 - x, y$ |
| (ii) $1.5 - y, z, 1.5 - x$ | (v) $z, x, y$              |
| (iii) $y, z, x$            |                            |

the structure of triclinic  $\text{NaH}_2(\text{PW}_{12}\text{O}_{40}) \cdot (12-14)\text{H}_2\text{O}$ . The agreement between the anion structure in this salt and the structure that we have found is excellent. The atoms W, O(1), O(2), O(3), and O(4) in our structure are shifted 0.04, 0.19, 0.25, 0.21, and 0.17 Å, respectively, from Keggin's positions. Still, it is remarkable that the older structures from a small number of powder data are as close to the modern results as they are.

d'Amour & Allmann (1976) have also determined the structure of triclinic  $\text{H}_3(\text{PMo}_{12}\text{O}_{40}) \cdot (13-14)\text{H}_2\text{O}$  and made comparisons of its anion with our  $(\text{PW}_{12}\text{O}_{40}^{3-})$  anion and with the anion in 'tetragonal'  $\text{H}_3(\text{PMo}_{12}\text{O}_{40}^{3-}) \cdot (29-31)\text{H}_2\text{O}$  as determined by Strandberg (1975). Allmann (1976) later showed that Strandberg's compound is actually cubic and isomorphous with the compound  $\text{H}_3(\text{PW}_{12}\text{O}_{40}) \cdot 29\text{H}_2\text{O}$  (Noe-Spirlet *et al.*, 1975).

An independent determination of Strandberg's compound has also been reported (Clark & Hall, 1976).

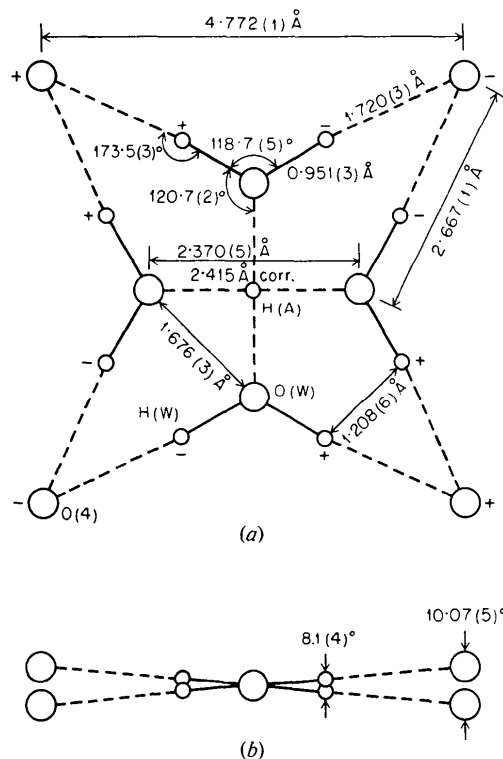


Fig. 2. (a) Detail from center of Fig. 1(b) showing the structure of the diaquahydrogen ion  $\text{H}_3\text{O}_2^+$  and its hydrogen-bonding to O(4) atoms of neighboring anions. Atom H(A) is on a  $42m$  site, and the  $\text{H}_3\text{O}_2^+$  ion (symmetry 222) is in twofold disorder about this site, as shown. Atoms marked with + signs are above the plane through the four O(W) sites, and those marked with - signs are below the plane. (b) View along the O(W) ··· H(A) ··· O(W) axis of the  $\text{H}_3\text{O}_2^+$  ion oriented vertically in (a), showing the twist through the O(W) ··· H(A) ··· O(W) axis. Angles shown are conformation angles about the axis. The figure does not take account of the possible disorder of O(W) about the twofold axis discussed in the last section of the paper.

Because of the relatively long distance, 2.46 Å, from Mo to O(1) (our notation) in their Keggin ion, Clark & Hall prefer to avoid the usual description of the ion as made up of 12 MoO<sub>6</sub> octahedra sharing edges, with a P atom in the central tetrahedron. They favor a description in terms of a clathrate structure in which 12 MoO<sub>5</sub> pyramids share edges to form a unit, Mo<sub>12</sub>O<sub>36</sub>, which encloses a guest PO<sub>4</sub><sup>3-</sup> ion, suggesting that such clathrate formation may be the essential basis of the formation of the heteropoly acids.

As we view the matter, however, there is not sufficient room within the Mo<sub>12</sub>O<sub>36</sub> unit or within the corresponding W<sub>12</sub>O<sub>36</sub> unit to contain a PO<sub>4</sub><sup>3-</sup> ion simply as a guest. The O(1)–O(3) distance (our notation) in the Clark & Hall PMo<sub>12</sub>O<sub>40</sub><sup>3-</sup> ion is 2.63 (2) Å; in (H<sub>5</sub>O<sub>2</sub><sup>+</sup>)<sub>3</sub>(PW<sub>12</sub>O<sub>40</sub><sup>3-</sup>) it is 2.591 (1) Å. Since these distances are about 0.2 Å less than the usually quoted O···O van der Waals separation and since there are 12 of them in each ion, it is highly unlikely that the ions could be stable without primary valence forces acting between the O(1) and the Mo or W atoms.

Another objection to the notion of clathrate structure in the heteropoly acid series is that it ignores the existence of the isopoly complexes, such as in metadodecatungstic acid (see discussion below of isomorphous 'pentahydrates') and in the paradodecatungstates (Evans, 1971; Evans & Rollins, 1976, and references therein). In these compounds the sixth O atom about each W atom cannot be assigned to a guest anion, as there is no such anion present.

Finally, the thermal ellipsoids shown in Fig. 1(a) do not suggest the freedom of motion that would be expected for a guest ion PO<sub>4</sub><sup>3-</sup>.

#### Hydrogen-bonding and packing

The hydrogen-bonding pattern, shown in Fig. 1(b), (c) and in Fig. 2, is extraordinary. The 24 half O atoms O(W) of the water molecules are arranged in six squares 1.676 Å on a side, centered on the 6-*d*-4̄2*m* sites of the cell. Associated with the 24 half O atoms are 48 half H atoms H(W) in general positions where they make good hydrogen bonds to 24 atoms O(4) at the unshared corners of the octahedra about the W atoms. At the center of each square of half O atoms is one of the protons H(A) from the ionization of the acid. There is just one H<sub>5</sub>O<sub>2</sub><sup>+</sup> ion at each 6-*d*-4̄2*m* site in the crystal; it may be oriented in either of two ways. The two possible orientations are shown most clearly in the center of the stereoscopic Fig. 1(b) and also in Fig. 2, where angles and distances involving the hydrogen bonds are given. In both orientations the ion is hydrogen-bonded to the same four atoms O(4). The H<sub>5</sub>O<sub>2</sub><sup>+</sup> ion is discussed in detail in the last section of the paper.

The structure may be thought of as made up of two different interpenetrating substructures of anions and

Table 3. *Some distances (Å) between atoms of the two different interpenetrating substructures and distances from the 3̄*m* centers to neighboring oxygen atoms*

Distances between anion and H <sub>5</sub> O <sub>2</sub> <sup>+</sup>	
O(2)···H(W)	3.13
O(2)···O(W)	3.32
O(3)···H(W)	2.88
O(3)···O(W)	3.13
Distances between anions related by centers 4- <i>c</i> -3̄ <i>m</i> ( $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ; etc.)	
O(2)···O(2)	4.74
O(4)···O(4)	3.34
O(2)···O(4)	3.40
Center···O(2)	2.70*
Center···O(4)	2.98*
Distances between anions related by centers 4- <i>b</i> -3̄ <i>m</i> (0, 0, 0; etc.)	
O(3)···O(3)	3.60
O(4)···O(4)	3.89
O(3)···O(4)	3.21
Center···O(3)	2.23*
Center···O(4)	3.38*

\* Six such neighbors about each center.

disordered H<sub>5</sub>O<sub>2</sub><sup>+</sup> cations with space-group symmetry *P*4̄3*m*, the two having no hydrogen-bonding between them. A portion of one of the two cubic substructures is shown in Fig. 1(b). Fig. 1(c) shows most of what is in Fig. 1(b), plus one anion and four disordered H<sub>5</sub>O<sub>2</sub><sup>+</sup> units of the second substructure. The second substructure is related to the first by inversion through the origin.

Table 3 shows some distances of interest between atoms belonging to the two different substructures and also distances from the 3̄*m* centers to neighboring atoms. Although the structure is somewhat 'open' at both kinds of 3̄*m* site, it is not surprising that we find no water molecules at the 4-*c*-3̄*m* centers where Keggin placed them; the spaces available are not quite large enough. Because Keggin's atom O(2) was misplaced somewhat, his apparent distance from each center to each O(2) neighbor was 2.93 Å rather than the 2.70 Å that we find, justifying to some degree his placement of the water molecules.

#### Relation to structures of isomorphous 'pentahydrates'

The details of structure near the atoms O(4) in 12-phosphotungstic acid hexahydrate allow us to infer something about the locations of the extra H atoms in the so-called pentahydrates of 12 silicotungstic acid, 12-borotungstic acid, and metadodecatungstic acid. We conclude that these 'pentahydrates' are all hexahydrates, to be properly formulated as (H<sub>5</sub>O<sub>2</sub><sup>+</sup>)<sub>3</sub>-(HSiW<sub>12</sub>O<sub>40</sub><sup>3-</sup>), (H<sub>5</sub>O<sub>2</sub><sup>+</sup>)<sub>3</sub>-(H<sub>2</sub>BW<sub>12</sub>O<sub>40</sub><sup>3-</sup>), and (H<sub>5</sub>O<sub>2</sub><sup>+</sup>)<sub>3</sub>-(H<sub>3</sub>H<sub>2</sub>W<sub>12</sub>O<sub>40</sub><sup>3-</sup>), since they have been shown from

powder diffraction photographs to be isomorphous with 12-phosphotungstic acid hexahydrate (Signer & Gross, 1934; Illingworth & Keggin, 1935). The extra H atoms in the 12-borotungstic and 12-silicotungstic acids are replaceable, as are three of those in metatungstic acid. These replaceable H atoms must be chemically bonded to O(4) atoms – randomly distributed on the 12 O(4) atoms of each anion. There should be ample room for these extra atoms, on the assumption that spatial relations in these isomorphous compounds are about the same as in 12-phosphotungstic acid hexahydrate. In the latter compound each O(4) atom has as near neighbors in other anions an O(3) at 3.21 Å and an O(2) at 3.40 Å, both on the mirror plane common to all three atoms, and also two O(4) atoms at 3.34 Å and two O(4) atoms at 3.89 Å. The preferred position for each extra H would be near O(3) on the common mirror plane, since the O(4)···O(3) distance, 3.21 Å, is almost short enough to suggest a weak hydrogen bond and the angle W–O(4)···O(3) of 102.9° favors this kind of interaction. However, the interaction may be so weak that there is rotational disorder about the W–O(4) axis. It might be possible to ‘see’ these H atoms by use of neutron diffraction if a fully deuterated single crystal of metadodecatungstic acid hexahydrate could be grown. The fractional occupancy of H on each O(4) would be  $\frac{1}{4}$  (compare with  $\frac{1}{12}$  for the silicotungstic acid), which with the higher-magnitude scattering length of deuterium ( $0.667 \times 10^{-12}$  cm) might allow the deuterium atoms to be seen in a difference map even if there were rotational disorder.

Possible positions for the two nonreplaceable H atoms in metadodecatungstic acid have been discussed in the literature (see, for example, Schott & Harzdorf, 1956; Pope & Varga, 1966). Schott & Harzdorf proposed that there are hydrogen bonds O(1)–H···O(1) on two opposite edges of the tetrahedron of O(1) atoms inside the anion. There would then be disorder in the sense that there are three pairs of opposite edges and four arrangements for asymmetric hydrogen bonds for each pair. The PMR data of Pope & Varga are consistent with the hydrogen-bonded tetrahedron of O(1) atoms. Since the O(1)···O(1) edge distance is 2.50 Å in 12-phosphotungstic acid hexahydrate, one may expect a fairly strong hydrogen bond between O(1) atoms in the metatungstic acid, even though the O(1)···O(1) distance there may be somewhat larger because of the absence of the usual hetero atom at the center of the tetrahedron. These interior H atoms should be observable in neutron diffraction, especially if the deuterated acid were to be studied.

#### *Relation to structurally similar salts of 12-heteropoly acids*

From the details of the structure of 12-phosphotungstic acid hexahydrate we can also make inferences

about the structure and water content of a wide variety of salts of 12-heteropoly acids with three univalent cations per anion, such as the Cs salts  $\text{Cs}_3(\text{PW}_{12}\text{O}_{40})$ ,  $\text{Cs}_3(\text{HSiW}_{12}\text{O}_{40})$ ,  $\text{Cs}_3(\text{H}_2\text{BW}_{12}\text{O}_{40})$ , and  $\text{Cs}_3(\text{H}_3\text{H}_2\text{W}_{12}\text{O}_{40})$ , which were studied by Santos (1935). Santos inferred from powder diffraction photographs that these salts have the same basic structure as Keggin’s 12-phosphotungstic acid ‘pentahydrate’ but that the three Cs ions replace the three waters per anion that Keggin placed at the 6–*d*– $42m$  sites. The question was left open as to whether the salts contain Keggin’s other two water molecules on 4–*c*– $3m$  sites. Our results show that each cesium ion must replace one  $\text{H}_5\text{O}_2^+$  ion, or in effect two molecules of water, so that there is no reason to think any water is left. There is, in any case, even less room for the extra water in these salts than in the 12-phosphotungstic acid hexahydrate, because the anions are closer together as a result of replacement of  $\text{H}_5\text{O}_2^+$  ions by cesium ions. If we assume, as is reasonable, that in  $\text{Cs}_3(\text{PW}_{12}\text{O}_{40})$  the anions are identical in shape, size, and orientation with those in the acid hexahydrate but use Santos’s cell translation of 11.830 Å for the salt, we calculate that each 4–*c*– $3m$  site is surrounded by six O(2) atoms at 2.58 Å instead of 2.70 Å as in the acid. The situation must be nearly the same in the acid Cs silico-, boro-, and metatungstates, which have cell translations between 11.777 and 11.832 Å. In these acid salts, the O(4)···O(3) distance near each 4–*b*– $3m$  site is reduced to 2.94–2.98 Å, depending on the cell translation, making hydrogen-bonding involving the acid H atoms more likely than in the corresponding hexahydrates of the acids. The Cs ions each have four equivalent O(4) neighbors at 3.10–3.14 Å (close to the sum of the van der Waals radii of 1.69 Å for  $\text{Cs}^+$  and 1.40 Å for O), four equivalent O(3) neighbors at 3.30–3.32 Å and four equivalent O(2) neighbors at 3.34–3.36 Å.

These cesium salts and cesium salts of similar structure involving other hetero atoms (Brown & Mair, 1958, 1962*a,b*; Brown, 1962*a,b*) are formulated in Evans’s (1971) review article as dihydrates, apparently simply as a result of Keggin’s error in assigning water molecules to the 4–*c*– $3m$  sites. We believe that all of the numerous salts of 12-heteropoly acids that have been reported to have the same basic structure as 12-phosphotungstic acid hexahydrate [see also: Illingworth & Keggin (1935); Ferrari & Nanni (1939)] are actually anhydrous salts. We specifically include several salts tabulated by Evans as tetrahydrates. For these there is evidence from chemical analysis (Ferrari & Nanni, 1939) that the water content varies from about four (usually slightly more) molecules per anion at room temperature to zero molecules at 140°C without changes in the unit-cell translations. Since there is no room in these salt structures for any water, we conclude that the water found at room temperature was water retained in the fine powders by surface forces.

*The diaquahydrogen ion, H<sub>5</sub>O<sup>+</sup><sub>2</sub>: alternative descriptions*

The H<sub>5</sub>O<sup>+</sup><sub>2</sub> ion (see Fig. 2) apparently has the symmetry of point group 222. It is distorted from the planar configuration of symmetry *mmm* by a twist of only 8.1(4)° about the O...H...O axis. No other H<sub>5</sub>O<sup>+</sup><sub>2</sub> ion having this geometry is known to us. The other known structures of H<sub>5</sub>O<sup>+</sup><sub>2</sub> ions which have been determined with any degree of reliability [for references see: Bell, Christoph, Fronczek & Marsh (1975); Lundgren & Tellgren (1974)] display pyramidal geometry for the O atoms instead of the planar configurations we find. They also have staggered conformations about the O...O axis.

The other striking features of this H<sub>5</sub>O<sup>+</sup><sub>2</sub> ion are the shortness of the internal hydrogen bond O(W)...H(A)...O(W) and the unusually large mean-square amplitude of vibration of O(W) perpendicular to the mean plane of the ion. The O(W)...H(A)...O(W) distance is only 2.370(5) Å, uncorrected for thermal motion. The perpendicular mean-square amplitude for O(W) is 0.0844 Å<sup>2</sup>, considerably exceeding the corresponding quantities 0.0449 and 0.0678 Å<sup>2</sup> for H(A) and H(W) respectively. These mean-square amplitudes may be interpreted as indicating significantly correlated antiparallel motions of the two O(W) atoms perpendicular to the mean plane, thereby implying a correction to the O(W)...H(A)...O(W) distance, which can be estimated by the following argument.

Consider the observed mean-square amplitudes of O(W) and H(A) in the direction perpendicular to the mean plane of H<sub>5</sub>O<sup>+</sup><sub>2</sub> to be sums of contributions from three modes of vibration: (1) libration-antiparallel O(W) motion, stationary H(A), (2) bending-parallel O(W) motion antiparallel to H(A) motion, (3) translation-parallel O(W) motion parallel to H(A) motion.

For H(A), libration contributes nothing. The bending contribution may be estimated from a ground-state harmonic-oscillator model, for which the mean-square amplitude is given by  $\bar{q}^2 = h/(8\pi^2 c \bar{\nu} \mu)$ , in which  $h$  is Planck's constant,  $c$  the velocity of light,  $\mu$  the oscillator reduced mass, and  $\bar{\nu}$  the oscillator wave number. We may take  $\bar{\nu} = 1200 \text{ cm}^{-1}$ , approximately the value for the bending mode of the bifluoride ion in KHF<sub>2</sub> (Newman & Badger, 1951) but not critical to our result. Then, taking  $\mu$  to be 32/33 the mass of the H atom, we obtain for the mean-square displacement of H from its mean site in bending motion

$$\bar{X}^2 [\text{H(A), bending}] = (32/33)^2 \bar{q}^2 = 0.0136 \text{ \AA}^2.$$

The translational contribution for H(A) may now be obtained by difference:

$$\begin{aligned} \bar{X}^2 [\text{H(A), translation}] &= \bar{X}^2 [\text{H(A), obs}] - \bar{X}^2 [\text{H(A),} \\ &\quad \text{bending}] \\ &= 0.0313 \text{ \AA}^2. \end{aligned}$$

For O(W), the translational contribution is equal to that for H(A). The bending contribution is negligible, being the value for H(A) multiplied by  $\sim 1/32^2$ , the square of the appropriate mass ratio. Thus, the librational contribution can be obtained by the difference:

$$\begin{aligned} \bar{X}^2 [\text{O(W), libration}] &= \bar{X}^2 [\text{O(W), obs}] - 0.0313 \\ &= 0.0531 \text{ \AA}^2. \end{aligned}$$

The corrected O(W)...H(A)...O(W) distance (Busing & Levy, 1964) is thus

$$2 \times [(2.370/2)^2 + 0.0531]^{1/2} = 2.414 \text{ \AA}.$$

In principle, a further correction would arise from motion in the mean plane of the H<sub>2</sub>O<sup>+</sup><sub>2</sub> ion perpendicular to the O...O link; however, the observed O(W) mean-square amplitude (0.0232 Å<sup>2</sup>) in this direction is too small compared to that for H(A) (0.0442 Å<sup>2</sup>) to furnish an appreciable additional correction.

The valence angle H(W)—O(W)—H(W) of the water molecule is 118.7(5)°, markedly larger than the angle 104.52° in gaseous water (Benedict, Gailar & Plyler, 1956) and larger than that usually found in crystalline hydrates. The enlarged valence angle and the unusually short internal hydrogen bond may be related to the apparent fact that the whole diaquahydrogen ion H<sub>5</sub>O<sup>+</sup><sub>2</sub> is approximately planar, with the internal hydrogen bond collinear with the bisector of the valence angle.

Theoretical studies of the isolated H<sub>2</sub>O<sup>+</sup><sub>2</sub> ion (Kramer & Diercksen, 1970; Kollman & Allen, 1970; Newton & Ehrenson, 1971) seem to favor slightly the staggered  $\bar{4}2m$  (*D*<sub>2d</sub>) configuration as most stable, in disagreement both with the geometry we find and also with the different geometry reported from other crystal structure analyses.

One can reasonably interpret the apparent 222 symmetry of the H<sub>5</sub>O<sup>+</sup><sub>2</sub> ion and the thermal parameters discussed above in a different way, which brings our geometrical description more into harmony with the descriptions from other studies. The large mean-square amplitude of O(W) perpendicular to the mean plane of the H<sub>5</sub>O<sup>+</sup><sub>2</sub> ion can be ascribed to disorder of the O(W) atom in positions slightly displaced from the twofold axis on which we have placed it. By moving O(W) off the axis in the *x* direction and reducing the *U*<sub>11</sub> thermal parameter and holding it fixed,\* we were able to obtain slightly lower values of *R*<sub>w</sub>(*F*<sup>2</sup>) and  $\sigma_1$  in further least-squares refinement. The best fit [*R*(*F*) = 0.034, *R*(*F*<sup>2</sup>) = 0.030, *R*<sub>w</sub>(*F*<sup>2</sup>) = 0.59,  $\sigma_1 = 1.120$ ] was obtained when *U*<sub>11</sub> was fixed at 0.0374 Å<sup>2</sup>. There was no improvement in agreement for the discrepant data discussed above under *Neutron refinement*. The *x* coordinate of O(W) refined to 0.7656(2), corresponding to a shift of

\* Because of high correlation, it was not possible to refine successfully both *x* and *U*<sub>11</sub>.



0.190 Å from the twofold axis; other parameters were not changed significantly from those in Table 1. According to the *R*-factor ratio test (Hamilton, 1965; *International Tables*, 1974), the hypothesis that the equilibrium position of atom O(*W*) is on the twofold axis may be rejected at less than the 0.005 level of probability. This would imply pyramidal geometry for O(*W*), as has been observed for other examples of  $\text{H}_5\text{O}_2^+$  ions. However, in view of the assumptions as to linearity involved in the use of the *R*-factor ratio test, no clear-cut choice between the two ways of interpreting the thermal parameters seems possible. If the disorder exists, it is likely not to be static but rather dynamic disorder of inversion of the pyramidal O(*W*) atom.

If the equilibrium O(*W*) position is 0.190 Å off the twofold axis, the O(*W*)...H...O(*W*) distance (assuming linearity) is 2.400 Å, the O—H distance is 0.969 Å, and the H—O—H angle is 115.1° (all uncorrected for thermal motion). The 0.190 Å displacement implies a rather flat pyramid, with the O...H direction deviating only about 30° from the bisector of the H—O—H angle.

In either of the alternative descriptions the hydrogen bond O(*W*)...H(*A*)...O(*W*) at ~2.40 Å is one of the shortest ever observed involving O atoms.

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