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Dodecatungstophosphoric Acid-21-Water by Neutron Diffraction*

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Abstract. $H_3PW_{12}O_{40}.21H_2O$, orthorhombic, $Pcca$, $Z = 4$, $a = 20{\cdot}788$ (10), $b = 13{\cdot}086$ (3), $c = 18{\cdot}879$ (5) Å [at 22°C, λ(Mo $K\alpha$) = 0·70926 Å], $D_o = 4{\cdot}17$, $D_c = 4{\cdot}21$ g cm^{-3}. Keggin anions form a layer near $y = 0$. Each has $\bar{4}3m$ pseudosymmetry with the central P atom on a twofold axis $x = \frac{1}{4}, y = 0$, at $z = 0{\cdot}44585$ (8). A pseudo $\bar{4}$ axis makes an angle of 20·42 (3)° with the x direction. Eighteen water O atoms form a second layer with $0{\cdot}32 \leq y \leq 0{\cdot}68$, and three others penetrate into the anion region.

Introduction. Crystals were prepared by room-temperature evaporation of solutions of $H_3PW_{12}O_{40}$ in aqueous nitric acid. A neutron-diffraction sample measuring 1·25 × 4·18 × 3·75 mm and weighing 83 mg was mounted in a thin-walled quartz tube together with some powdered hydrate to protect it from loss of water.

Integrated intensities were measured for neutrons with $\lambda = 1{\cdot}2455$ Å using $\omega/2\theta$ scans. 8348 reflections were measured and corrected for absorption using $\mu = 1{\cdot}70$ cm^{-1}. The correction factors ranged from 1·221 to 1·779. Equivalent observations were averaged to yield the 3951 unique reflections accessible with $2\theta < 90°$. Each intensity was converted to F_o^2 in the usual way, and its standard error was computed as $\sigma = [\sigma_c^2 + (0{\cdot}03\ F_o^2)^2]^{1/2}$, where σ_c is the contribution of counting statistics. Only 1634 observations exceed 2σ, and the least-squares refinements described below were based on the 1327 reflections for which both F_o^2 and F_c^2 exceed 2σ. An isotropic extinction coefficient was adjusted, but only the two strongest reflections showed a significant effect.

The structure was solved by direct methods, the E map yielding all 27 anion atoms and two of the water O atoms. Fourier syntheses interspersed with least-squares refinements revealed the remaining water O atoms and probable H sites. Many of the latter appear to be disordered, and the water O atoms show large apparent thermal motion, which is probably associated with this fact. Because of this large thermal motion and the low occupancy and near overlap of many of the H sites it was not possible to make a conventional

Table 1. *Fractional coordinates* (× 10^4) *for* $H_3PW_{12}O_{40}.21H_2O$ *with standard errors in parentheses*

	X	Y	Z
P	2500	0	4457(7)
W(1)	3217(5)	2467(7)	4503(5)
W(2)	953(5)	1128(7)	4413(6)
W(3)	3617(5)	729(8)	5802(5)
W(4)	1352(5)	-606(8)	3122(5)
W(5)	2128(5)	1816(8)	5794(5)
W(6)	2041(5)	1764(8)	3123(5)
O(11)	2749(4)	863(7)	4926(4)
O(12)	1955(4)	392(6)	3988(4)
O(21)	2824(5)	1124(7)	2879(4)
O(22)	1784(4)	526(7)	6029(4)
O(23)	3503(4)	-1821(7)	5061(5)
O(24)	2478(5)	-2422(6)	3856(4)
O(25)	967(4)	13(7)	5058(4)
O(26)	3646(4)	1606(7)	3848(5)
O(31)	2923(4)	1442(7)	6214(4)
O(32)	1595(5)	655(7)	2699(4)
O(33)	2598(5)	2769(7)	5237(4)
O(34)	1270(5)	1992(7)	3682(4)
O(35)	3757(5)	1955(7)	5232(4)
O(36)	753(4)	148(7)	3686(4)
O(41)	3536(5)	3633(6)	4354(5)
O(42)	216(4)	1686(8)	4567(5)
O(43)	4208(4)	856(8)	6408(5)
O(44)	859(5)	-1119(8)	2507(5)
O(45)	1791(5)	2580(7)	6410(4)
O(46)	1968(5)	2729(7)	2521(5)
O(W1)	4772(6)	1521(10)	1213(6)
O(W2)	4960(8)	3258(11)	936(8)
O(W3)	1603(5)	4131(7)	4379(6)
O(W4)	2500	5000	3434(7)
O(W5)	3358(5)	4003(9)	2530(6)
O(W6)	4539(7)	4057(13)	3034(9)
O(W7)	468(8)	3681(12)	3384(8)
O(W8)	0	1782(9)	2500
O(W9)	513(7)	3609(9)	809(8)
O(W10)	1681(6)	4194(9)	1511(6)
O(W11)	2500	5000	579(16)
O(W12)	4218(6)	4631(9)	396(6)
H(1,1)	4550	1363	1626
H(1.2)	4987	1014	1106
H(2,1)	4858	2662	970
H(2,2)	5139	3428	1320
H(2,3)	4656	3564	904
H(3,1)	1712	3435	4353
H(3,2)	1176	4195	4486
H(3.3)	1682	4430	3965
H(3,4)	1831	4424	4707
H(4,1)	2729	4527	3136
H(4,2)	2197	4629	3737
H(5,1)	3263	3465	2257
H(5,2)	3051	4064	2886
H(5.3)	3748	3916	2726
H(5,4)	3358	4595	2255
H(6,1)	4545	4651	3167
H(6,2)	4142	3938	2857
H(6,3)	4820	4005	2671
H(7,1)	814	3704	3576
H(7,2)	446	3126	3183
H(7,3)	211	3681	3678
H(8,1)	229	1366	2189
H(8,2)	275	2187	2746
H(9.1)	561	3051	632
H(9.2)	222	3567	1071
H(9,3)	832	3725	1046
H(10,1)	1790	3678	1771
H(10.2)	1970	4306	1210
H(10.3)	1324	4060	1296
H(10.4)	1634	4713	1769
H(11.1)	2626	4552	305
H(11.2)	2292	4522	699
H(12,1)	4386	5069	305
H(12.2)	4486	4136	468
H(12.3)	3965	4473	65
H(12,4)	4016	4734	748

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unconstrained least-squares refinement of the H positions. Instead, independent coordinates and anisotropic temperature factors were refined only for the non-hydrogen atoms. H coordinates were varied, but O—H distances and H—O—H angles were pushed toward reasonable values using the method of Waser (1963). The anisotropic thermal motion of each H atom was constrained to be a linear combination of the motions of the two O atoms between which it forms a hydrogen bond plus an adjustable isotropic contribution, which is the same for all H atoms. Occupancies of the H sites were refined subject to the limitations: (*a*) the total number of H atoms in the asymmetric unit is 22·5, (*b*) no O atom can have less than 2·0 H atoms of its own, and (*c*) no hydrogen bond can include a total of more than 1·0 H atom in adjacent disordered sites. The final refinement with 463 variables was made by alternately adjusting groups of 259 and 278 parameters, with 74 variables common to the two blocks. The resulting coordinates are given in Table 1.* The conventional discrepancy factors are: $R(F) = 6{\cdot}2\%$ and $R(F^2) = 9{\cdot}5\%$ for the 1327 reflections included. A final structure factor calculation for all 3951 data showed only two reflections with $\Delta \equiv |F_o^2 - F_c^2| > 4\sigma$ and only 39 with $\Delta > 3\sigma$. Neutron scattering lengths used were $b_{\rm P} = 0{\cdot}511$, $b_{\rm W} = 0{\cdot}477$, $b_{\rm O} = 0{\cdot}5804$, and $b_{\rm H} = -0{\cdot}3739$ (all in units of 10^{-12} cm).

After the refinement was completed two further cycles of least squares were performed in which the

Table 2. *Cartesian coordinates and interatomic distances (both in Å) for idealized* $\bar{4}3m$ *anion*

	x,*y*	*z*		*d*
P	0	0	P—O(1)	1·527 (5)
W	2·513 (2)	0·090 (4)	W—O(1)	2·439 (4)
O(1)	0·882 (3)	0·882 (3)	W—O(2)	1·899 (3)
O(2)	1·141 (2)	−2·968 (3)	W—O(3)	1·911 (3)
O(3)	1·465 (2)	3·329 (3)	W—O(4)	1·693 (4)
O(4)	3·692 (2)	−0·202 (4)		

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33193 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

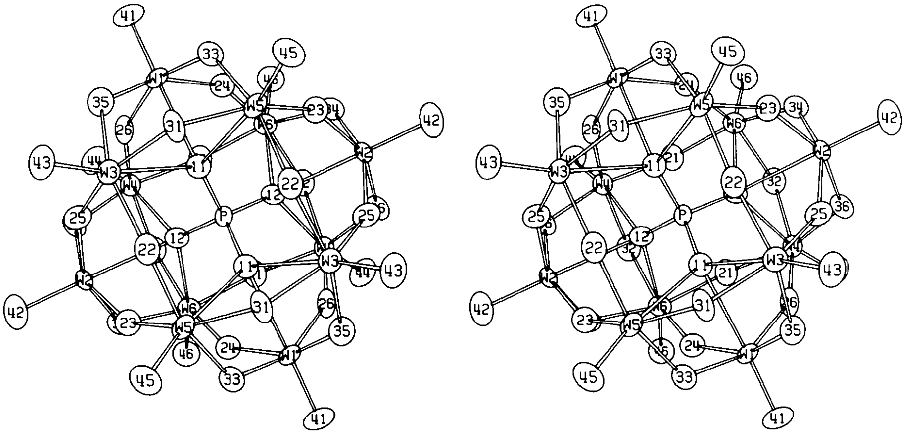

Fig. 1. Stereoscopic view of the $PW_{12}O_{40}^{3-}$ anion looking approximately down the crystallographic twofold axis. The O atoms are identified by their numbers only.

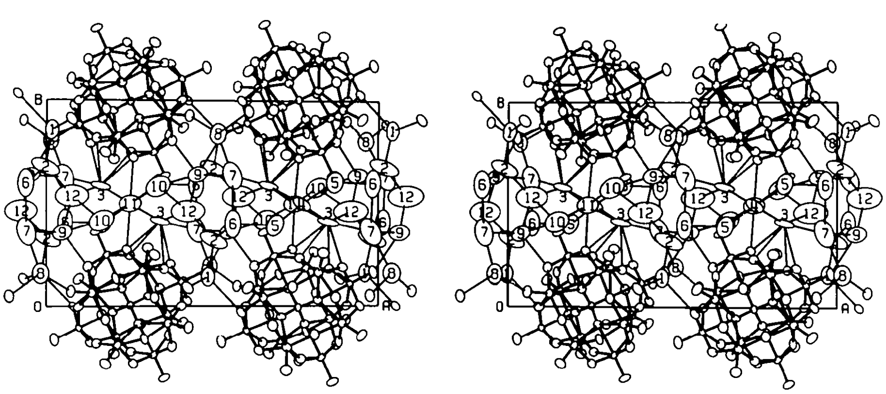

Fig. 2. Stereoscopic view of $H_3PW_{12}O_{40}.21H_2O$ looking down the *c* axis. The water O atoms are numbered and the lines connecting them represent most of the hydrogen bonds listed in Table 3. The anions to the left have the same orientation as that in Fig. 1.

Table 3. *Hydrogen bonds and* O—O *contacts in the water layer*

A(H) is the occupancy factor for hydrogen, O—H and O—O′ are distances (Å) and *α* is the hydrogen-bond angle H—O—O′ (°).

O———H·······H′———O′	*A*(H)	*A*(H′)	O–H	O–O′	*α*
O(*W*1)–H(1,1) ··············O(44)	1·00		0·93	2·82	3
O(*W*1)–H(1,2) ··············O(36)	1·00		0·83	2·99	20
O(*W*1)·····················O(42)				3·11	
O(*W*1)·····················O(26)				3·29	
	2·00				
O(*W*2)–H(2,1) ··············O(*W*1)	1·00		0·81	2·36	10
O(*W*2)–H(2,2) ··············O(*W*6)	1·00		0·84	2·44	10
O(*W*2)–H(2,3)···H(12,2)——O(*W*12)	0·50	0·50	0·75	2·58	25
O(*W*2) ·····················O(41)				3·21	
	2·50				
O(*W*3)–H(3,1) ··············O(24)	0·71		0·94	3·10	30
··············O(34)				3·17	34
··············O(33)				3·18	48
··············O(23)				3·29	32
O(*W*3)–H(3,2)···H(12,3)–O(*W*12)	0·44	0·31	0·91	2·65	36
O(*W*3)–H(3,3)···H(4,2)––O(*W*4)	0·33	0·49	0·89	2·82	31
O(*W*3)–H(3,4)···H(11,1)–O(*W*11)	0·52	0·48	0·87	3·15	5
O(*W*3) ····················O(41)				2·94	
	2·00				
O(*W*4)–H(4,1)···H(5,2)——O(*W*5)	0·51	0·49	0·96	2·79	13
O(*W*4)–H(4,2)···H(3,3)——O(*W*3)	0·49	0·33	0·98	2·82	6
O(*W*4) ·····················O(41)				3·29	
	1·00 ×2				
O(*W*5)–H(5,1) ··············O(45)	1·00		0·89	2·83	14
O(*W*5)–H(5,2)···H(4,1)——O(*W*4)	0·49	0·51	0·93	2·79	23
O(*W*5)–H(5,3)···H(6,2)——O(*W*6)	0·18	0·82	0·90	2·63	9
O(*W*5)–H(5,4)···H(10,4)——O(*W*10)	0·62	0·38	0·93	3·05	6
	2·29				
O(*W*6)–H(6,1) ··············O(*W*7)	0·68		0·82	3·03	5
O(*W*6)–H(6,2)···H(5,3)——O(*W*5)	0·82	0·18	0·90	2·63	8
O(*W*6)–H(6,3)···H(6,3)——O(*W*6)	0·50	0·50	0·90	2·78	5
O(*W*6) ·····················O(41)				3·30	
	2·00				
O(*W*7)–H(7,1) ··············O(*W*3)	0·84		0·80	3·07	15
O(*W*7)–H(7,2)···H(8,2)——O(*W*8)	0·84	0·18	0·82	3·15	16
··············O(34)				2·82	55
O(*W*7)–H(7,3)···H(9,2)——O(*W*9)	0·49	0·51	0·77	2·55	10
	2·17				
O(*W*8)–H(8,1) ··············O(43)	1·00		0·93	2·90	11
O(*W*8)–H(8,2)···H(7,2)——O(*W*7)	0·18	0·84	0·91	3·15	22
	1·18 ×2				
O(*W*9)–H(9,1) ··············O(35)	1·00		0·81	2·86	25
··············O(42)				3·02	38
O(*W*9)–H(9,2)···H(7,3)——O(*W*7)	0·51	0·49	0·78	2·55	7
O(*W*9)–H(9,3)···H(10,3)——O(*W*10)	0·49	0·37	0·82	2·87	7
	2·00				
O(*W*10)–H(10,1)············O(46)	0·93		0·86	2·77	9
O(*W*10)–H(10,2)···H(11,2)–O(*W*11)	0·37	0·63	0·84	2·67	13
O(*W*10)–H(10,3)···H(9,3)—O(*W*9)	0·37	0·49	0·86	2·87	4
O(*W*10)–H(10,4)···H(5,4)—O(*W*5)	0·38	0·62	0·84	3·05	6
	2·05				
O(*W*11)–H(11,1)···H(3,4)—O(*W*3)	0·48	0·52	0·82	3·15	26
············O(33)				3·00	36
O(*W*11)–H(11,2)···H(10,2)–O(*W*10)	0·63	0·37	0·79	2·67	32
············O(33)				3·00	42
	1·11 ×2				

Table 3 (*cont.*)

O——H········ H′——O′	*A*(H)	*A*(H′)	O–H	O–O′	*n*
O(*W*12)–H(12,1)············O(*W*9)	0·99		0·69	2·50	37
O(*W*12)–H(12,2)···H(2,3)—O(*W*2)	0·50	0·50	0·87	2·58	14
O(*W*12)–H(12,3)···H(3,2)—O(*W*3)	0·31	0·44	0·84	2·65	2
O(*W*12)–H(12,4)············O(*W*10)	0·39		0·80	3·21	21
	2·19				

only variables were the 11 parameters of a model which forced the coordinates of the anion atoms to have $\bar{4}3m$ symmetry. The results are given in Table 2 along with the interatomic distances in this idealized anion. The largest displacement of an idealized atom from its independently refined position is 0·054 Å and the r.m.s. displacement of all atoms is 0·022 Å.

The computer programs used were those listed by Lisensky, Johnson & Levy (1976).

Discussion. X-ray studies of this substance were first made by Kraus (1936, 1940), but his tentative determination of space group *Pccm* is not correct. Fig. 1 shows the anion geometry and Fig. 2 illustrates the overall structure as described in the *Abstract*.

The Cartesian coordinates of the idealized anion (Table 2) show small but significant differences from those found in the 6-hydrate (Brown, Noe-Spirlet, Busing & Levy, 1977) and the 29-hydrate (Noe-Spirlet, Brown, Busing & Levy, 1975). However, the idealized interatomic distances are in good agreement with those in these two structures.

Three water O atoms occupy special positions on twofold axes: O(*W*4) and O(*W*11) at 4(*e*) and O(*W*8) at 4(*c*). The remaining nine water O atoms are in general positions, making a total of 21 water molecules in two asymmetric units. Table 3 lists all the O—O contacts less than 3·3 Å, most of which can be considered to be hydrogen bonds. Many of the uncorrected O—O distances appear to be quite short, but this is related to the large apparent thermal motion of these water O atoms. For example, the distance O(*W*1)—O(*W*2) which is listed as 2·36 Å is estimated to be 2·52 Å assuming independent motion of the two atoms (Busing & Levy, 1964).

Also described in Table 3 are the 36 H atom sites and the hydrogen bond in which each participates. The table lists the occupancy factors, eight full and the rest partial, which account for a total of 22·5 H atoms in the asymmetric unit, or 45 in the formula. The acid protons are not distinguishable. These occupancy factors have nominal standard errors of about 0·05, but they depend upon the thermal motion assumed for the H atoms. Five O atoms have the minimum allowed total of 2·0 protons and the other seven have more, with a maximum of 2·50 for O(*W*2).

The calculated O—H distances tend toward the values which were used as observations in Waser's method. These ranged from 0·80 to 0·91 Å, depending on the thermal motion of the corresponding O(*W*). They should be considered as a description of the model, not as significant new information. All water H—O—H angles except those for O(*W*11) calculate to between 107 and 110°, again reflecting the slack constraints applied. The H—O(*W*11)—H angles were not constrained; they range from 78 to 147°.

Fig. 2 shows most of these hydrogen bonds and illustrates the variety of coordination arrangements found in the water layer. For example, O(*W*1) is ordered and strongly bonded to two anions, but O(*W*4) has a disordered tetrahedral coordination similar to that found in ice (Peterson & Levy, 1957). At least two kinds of five-membered rings can be seen.

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