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A Refinement of the Crystal Structure of $H_3PO_4.\frac{1}{2}H_2O$ with Neutron Diffraction Data

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The hydrogen positions in $H_3PO_4.\frac{1}{2}H_2O$ have been determined and the structure refined to $R_w=0{\cdot}022$, $R=0{\cdot}027$, with 1208 reflections of measurable intensity. The general features of the structure are as described by Mighell, Smith & Brown [*Acta Cryst.* (1969). B**25**, 776–781]. The two crystallographically discrete H_3PO_4 molecules are hydrogen bonded to each other and to the water molecule. The positions of the hydrogens of the water molecule appear to have been affected by $H\cdots H$ repulsion from the H_3PO_4 hydrogen atoms and the $O_w\text{–}H\cdots O$ (phosphate) hydrogen bonds are markedly non-linear. For P–O–H, the average P–O distance is 1·562 Å, the average O–H distance is 1·010 Å and the average P–O–H angle is 117°. Individual P–O–H angles range from 112·4° to 119·9°. In the water molecule, the average O–H distance is 0·997 Å, and the H–O–H angle is 106·0 (2)°. The four shortest $H\cdots H$ interactions range from 2·161 (3) to 2·290 (3) Å, and may imply $H\cdots H$ van der Waals bonding as in $Ca(OH)_2$.

Introduction

The general features of the crystal structure of $H_3PO_4.\frac{1}{2}H_2O$ were determined from X-ray photographic data by Mighell, Smith & Brown (1969). We have now determined the hydrogen positions and refined the structure with neutron data obtained from a single crystal.

Experimental

A few crystals of phosphoric acid hemihydrate triply crystallized from reagent-grade phosphoric acid were put in a 3 mm id quartz tube which was then sealed with epoxy resin. The crystals (melting point 29·3 °C) were fused into one large mass by successive meltings with no more than ~80% of the material being liquid at any one time. A single crystal was grown from the melt by applying heat where necessary from a low wattage soldering iron and monitoring crystal growth between crossed polaroids. The resulting crystal had a volume of ~25 mm³. The crystal data $a=7{\cdot}92$ (1), $b=12{\cdot}99$ (2), $c=7{\cdot}47$ (1) Å, $\beta=109{\cdot}9$ (1)°, space group $P2_1/a$, $Z=8$ as given by Mighell *et al.* were used here.

Two equivalent sets of reflections were measured with neutron radiation and a computer-controlled four-circle diffractometer (Alperin & Prince, 1970) in a procedure described by Prince (1972).

All reflections with $h\geq 0$ and with $2\theta<100°$ at a wavelength of 1·232 Å were measured by a procedure described previously (Prince, 1972). If a preliminary measurement of intensity at the peak position did not exceed background by at least $2\sigma(I)$, where $\sigma(I)$ is given by $(Ip+Ib)^{1/2}$ and Ip and Ib are the peak and background intensities, respectively, the reflection was considered to be immeasurable. The crystal rotated about the φ axis by as much as 0·2° in 8 h, so a sharp, low-angle reflection was measured at frequent intervals. The diffractometer was programmed to follow an automatic reorientation procedure if the intensity at the predicted peak position fell below a predetermined level. The few cases in which the effect of the slight misorientation on integrated intensity was not negligible were later remeasured. The integrated intensity of a standard reflection fell by about 10% during the six weeks duration of the measurements. Reflections measured within a given three day period were, therefore, scaled according to the mean intensity of the standard reflection during that period.

All reflections except those of the form $h0l$ with $h>0$ were measured in at least two symmetry-equivalent positions. Equivalent reflections $F_1(hkl)$ and $F_2(hkl)$ were merged to form a unique set, $F_{\rm av}(hkl)$; the agreement index, defined by $R=\sum|F_1(hkl)-F_2(hkl)|/\sum F_{\rm av}(hkl)$, was 0·020. Observable intensity was found for 1208 of the 1454 independent reflections within the limits of the data-collection scheme.

The parameters for the phosphorous and oxygen atoms as given by Mighell *et al.* were used to phase an F_o nuclear-density synthesis which revealed all the hydrogen positions. The complete structure was refined with isotropic temperature factors to $R_w=0{\cdot}11$, $R=0{\cdot}11$, with average shift/error = 2·2 and then with anisotropic temperature factors to $R_w=0{\cdot}022$, $R=0{\cdot}027$, with average shift/error = 0·01. The unpublished program *RFINE*2 written by L. W. Finger of the Carnegie Institute of Washington was used. R_w is defined as $[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$, R as $\sum||F_o|-|F_c||/\sum|F_o|$. The scattering lengths used were P: 0·51; O: 0·577; H: −0·372 (Neutron Diffraction Commission, 1969). The quantity minimized was $\sum w(|F_o|-|F_c|)^2$. Weights of $1/\sigma^2$, where σ is the standard deviation as estimated from counting statistics, were used in all refinements. Corrections were made for isotropic secondary extinction. The extinction factor, r in the notation of Zachariasen (1967), refined to the reasonable value of $0{\cdot}326\ (9)\times 10^{-4}$ cm. The standard deviation of an ob-

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servation of unit weight was 2·29. The 49 reflections with extinction factors less than 0·70 were rejected from the final cycles because the calculation of such extinction factors is beyond the validity range of the Zachariasen approximation (Cooper & Rouse, 1971). The largest peak in a subsequent difference synthesis corresponded to about $\frac{1}{30}$ of an oxygen atom and was attributed to the background. The largest correlation coefficient was 0·80 between the extinction and scale parameters. All other correlation coefficients were below 0·54. The parameters from the final refinement are given in Table 1.*

Discussion of the structure

The structure of $H_3PO_4.\frac{1}{2}H_2O$ is shown in Fig. 1. The asymmetric unit is two H_3PO_4 molecules and one water molecule. The H_3PO_4 molecules and water molecules lie in layers perpendicular to [010]. The description given by Mighell *et al.* is still valid in general terms and the reader is referred to their paper for an overall view.

The details of the H_3PO_4 and water molecules and their environments are given in Table 2 and are shown in Figs. 2, 3 and 4. The P–O(H) bond distances, where O(H) has a covalently attached hydrogen atom, average 1·560 Å for the $H_3P(1)O_4$ molecule, 1·563 Å for the $H_3P(2)O_4$ molecule and 1·562 Å for both molecules when the distances are corrected for riding motion (Busing & Levy, 1964). The P–O bonds with no hydrogen covalently attached to O average 1·495 Å. The O–H distances, corrected for riding motion, aver-

Table 1. *Atomic parameters in* $H_3PO_4.\frac{1}{2}H_2O$

All values are × 10^4 except the *y* coordinates of the non-hydrogen atoms which are × 10^5. Figures in parentheses are standard deviations in last significant digit as estimated in the final cycle of full-matrix least-squares calculations. Thermal parameters have the form $\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	4464 (1)	39810 (8)	2521 (1)	133 (5)	232 (5)	180 (5)	−21 (4)	56 (3)	10 (3)
O(1)	5940 (1)	36929 (8)	4319 (1)	154 (4)	376 (6)	267 (5)	−4 (4)	4 (3)	104 (4)
O(2)	4478 (2)	33689 (9)	740 (1)	474 (7)	311 (7)	291 (5)	−38 (5)	223 (5)	−61 (4)
O(3)	2594 (1)	38099 (8)	2680 (1)	142 (6)	479 (6)	283 (5)	−78 (4)	77 (4)	−3 (4)
O(4)	4589 (1)	51219 (7)	1963 (1)	223 (5)	241 (5)	288 (4)	−39 (4)	37 (4)	29 (4)
H(1)	4169 (3)	2631 (2)	662 (3)	559 (12)	373 (11)	460 (11)	−12 (9)	226 (9)	−76 (8)
H(2)	2518 (2)	3905 (1)	3994 (3)	241 (3)	508 (10)	402 (10)	−31 (7)	144 (7)	15 (7)
H(3)	4243 (2)	4519 (1)	7379 (2)	294 (9)	343 (9)	445 (9)	−37 (8)	141 (7)	2 (7)
P(2)	5800 (1)	13664 (7)	6403 (1)	134 (4)	196 (5)	189 (5)	21 (4)	72 (4)	−2 (3)
O(5)	7451 (1)	10129 (8)	6067 (1)	155 (4)	345 (5)	281 (5)	52 (4)	103 (3)	12 (3)
O(6)	5457 (1)	7075 (8)	7985 (1)	385 (5)	243 (5)	339 (5)	21 (4)	235 (4)	49 (4)
O(7)	4227 (1)	12599 (8)	4499 (1)	154 (6)	450 (6)	235 (5)	−17 (4)	46 (3)	−68 (4)
O(8)	5868 (1)	24986 (7)	7103 (1)	332 (5)	202 (5)	246 (5)	23 (4)	94 (4)	−14 (4)
H(4)	4784 (3)	1007 (1)	8758 (2)	431 (10)	371 (9)	393 (10)	15 (8)	245 (8)	23 (7)
H(5)	2951 (2)	1289 (1)	4483 (2)	217 (10)	498 (11)	366 (8)	−19 (7)	80 (6)	−67 (7)
H(6)	817 (2)	1992 (1)	6081 (3)	373 (9)	310 (9)	400 (10)	1 (7)	86 (7)	−22 (7)
O(9)	8658 (1)	36448 (8)	196 (1)	242 (6)	313 (5)	263 (5)	6 (4)	82 (4)	−30 (4)
H(7)	2420 (3)	1202 (2)	−392 (3)	326 (12)	918 (18)	598 (14)	−93 (11)	111 (10)	−22 (12)
H(8)	4065 (3)	938 (2)	1298 (3)	619 (13)	702 (14)	465 (12)	101 (11)	186 (10)	241 (11)

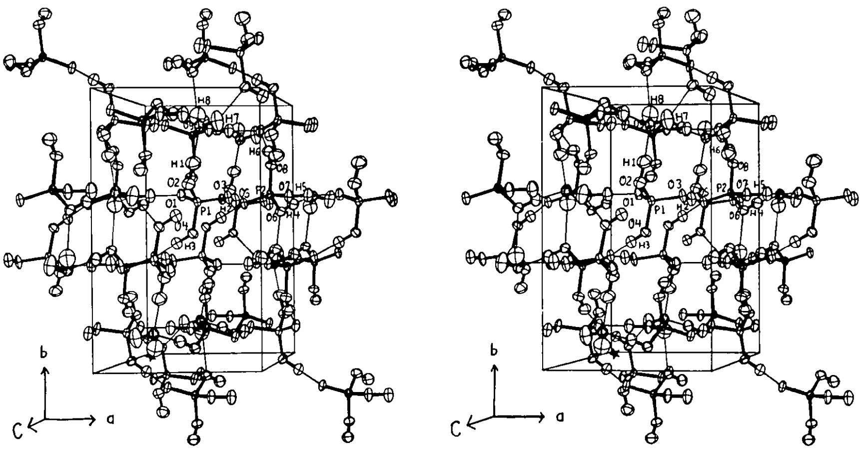

Fig. 1. A stereoscopic illustration of the crystal structure of $H_3PO_4.\frac{1}{2}H_2O$. A unique set of atoms ($2H_3PO_4$ molecules and 1 water molecule) is labelled. The P(2) atom and the water oxygen, O(9), are shaded. The origin of the crystallographic coordinate system is marked by *.

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* The table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30377 (6 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

age 1·010 Å for the $H_3P(1)O_4$ molecule and 1·009 Å for the $H_3P(2)O_4$ molecule. The P–O–H angles average 116·8° for $H_3P(1)O_4$ and 117·3° for the $H_3P(2)O_4$ group.

The environments of the two H_3PO_4 molecules are quite similar. Both phosphoryl oxygen atoms [O(1) and O(5)] are the acceptors in two hydrogen bonds. One O(H) atom on each H_3PO_4 molecule [O(4) and O(6)] is the acceptor in a weaker hydrogen bond from the water molecule. O(7) may be the acceptor of a very weak additional hydrogen bond from the water molecule to the $H_3P(2)O_4$ molecule. The $H_3P(1)O_4$ molecule donates a hydrogen bond to the phosphoryl oxygen of each of two neighboring $H_3P(2)O_4$ molecules; $H_3P(2)O_4$ donates two similar hydrogen bonds to $H_3P(1)O_4$ molecules. Each H_3PO_4 molecule donates its third hydrogen bond to the oxygen atom of the water molecule. The bonds to phosphoryl oxygens are stronger than those to the water molecule, consistent with the fact that phosphoric acid also exists in an anhydrous form. The crystal structure of anhydrous H_3PO_4 has been determined by Petersen (unpublished) from neutron diffraction and by Furberg (1955) and Smith, Brown & Lehr (1955) from X-ray diffraction. The hydrogen bonds between H_3PO_4 molecules in $H_3PO_4.\frac{1}{2}H_2O$ are almost linear.

The water molecule accepts one hydrogen bond from an $H_3P(1)O_4$ molecule and accepts a second hydrogen bond from an $H_3P(2)O_4$ molecule. It is the

Table 2. *Interatomic distances and angles in* $H_3PO_4.\frac{1}{2}H_2O$

i	*j*	*k*	D_{ij} (Å)		D_{jk} (Å)		D_{ik} (Å)	∠*ijk* (°)
O(1)	P(1)	O(2)	1·497 (1)	1·506^{RB}	1·553 (1)	1·568^{RB}	2·561 (1)	114·18 (1)
O(1)	P(1)	O(3)	1·497 (1)	1·506^{RB}	1·542 (1)	1·554^{RB}	2·518 (1)	111·84 (8)
O(1)	P(1)	O(4)	1·497 (1)	1·506^{RB}	1·551 (1)	1·559^{RB}	2·530 (1)	112·21 (8)
O(2)	P(1)	O(3)	1·553 (1)	1·568^{RB}	1·542 (1)	1·554^{RB}	2·476 (1)	106·22 (8)
O(2)	P(1)	O(4)	1·553 (1)	1·568^{RB}	1·551 (1)	1·559^{RB}	2·444 (1)	103·84 (8)
O(3)	P(1)	O(4)	1·542 (1)	1·554^{RB}	1·551 (1)	1·559^{RB}	2·503 (1)	107·99 (8)
P(1)	O(2)	H(1)	1·568^{RB}		0·985 (3)	0·999^{RB}	–	118·3 (1)
P(1)	O(3)	H(2)	1·554^{RB}		1·011 (2)	1·018^{RB}	–	115·7 (1)
P(1)	O(4)	H(3)	1·559^{RB}		1·002 (2)	1·012^{RB}	–	116·4 (1)
O(2)	H(1)	O(9)	0·999^{RB}		1·714 (2)		2·692 (2)*	171·5 (2)
O(3)	H(2)	O(5)	1·018^{RB}		1·571 (2)		2·581 (1)*	176·6 (2)
O(4)	H(3)	O(5′)	1·012^{RB}		1·583 (2)		2·580 (1)*	171·8 (2)
O(5)	P(2)	O(6)	1·485 (1)	1·493^{RB}	1·556 (1)	1·568^{RB}	2·499 (1)	110·45 (8)
O(5)	P(2)	O(7)	1·485 (1)	1·493^{RB}	1·545 (1)	1·557^{RB}	2·441 (1)	107·30 (7)
O(5)	P(2)	O(8)	1·485 (1)	1·493^{RB}	1·556 (1)	1·564^{RB}	2·560 (1)	114·66 (8)
O(6)	P(2)	O(7)	1·556 (1)	1·568^{RB}	1·545 (1)	1·557^{RB}	2·553 (1)	110·82 (8)
O(6)	P(2)	O(8)	1·556 (1)	1·568^{RB}	1·556 (1)	1·564^{RB}	2·469 (1)	105·02 (7)
O(7)	P(2)	O(8)	1·545 (1)	1·557^{RB}	1·556 (1)	1·564^{RB}	2·518 (1)	108·6 (17)
P(2)	O(6)	H(4)	1·568^{RB}		0·989 (2)	0·998^{RB}	–	119·7 (1)
P(2)	O(7)	H(5)	1·557^{RB}		1·008 (2)	1·017^{RB}	–	119·9 (1)
P(2)	O(8)	H(6)	1·564^{RB}		1·001 (2)	1·013^{RB}	–	112·4 (1)
O(6)	H(4)	O(9)	0·998^{RB}		1·675 (2)		2·659 (1)*	172·2 (2)
O(7)	H(5)	O(1)	1·017^{RB}		1·556 (2)		2·563 (1)*	176·2 (2)
O(8)	H(6)	O(1′)	1·013^{RB}		1·618 (2)		2·611 (1)*	170·3 (2)
H(7)	O(9)	H(8)	0·949 (3)	1·001^{RB}	0·946 (3)	0·993^{RB}	–	106·0 (2)
O(9)	H(7)	O(4)	1·001^{RB}		2·146 (3)		2·993 (1)*	147·9 (2)
O(9)	H(8)	O(6′)	0·993^{RB}		2·204 (3)		2·978 (1)*	138·3 (2)
O(9)	H(8)	O(7)	0·993^{RB}		2·387 (3)		3·092 (1)*	131·1 (2)

The large effects of thermal motion require corrections to the observed structural details. Because of inadequacies in the formulation of the model of scattering density, the reported standard deviations (in parentheses), which were estimated from the least-squares parameter values and the correlation matrix, can serve only as a guide to the accuracy of the reported details.

^{RB} Riding-model correction (Busing & Levy, 1964).
* These distances involve hydrogen bonds.

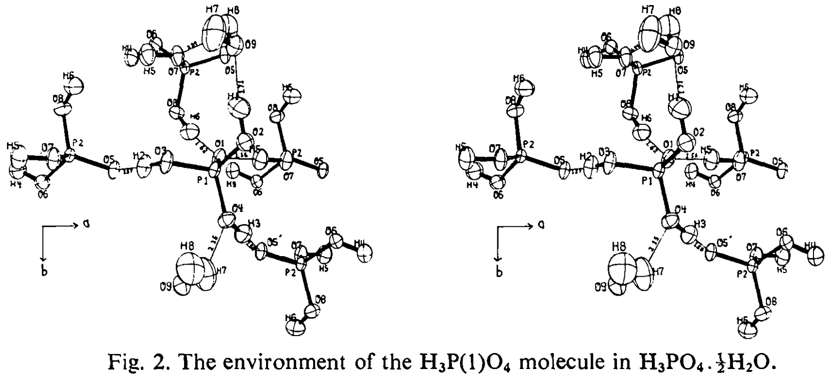

Fig. 2. The environment of the $H_3P(1)O_4$ molecule in $H_3PO_4.\frac{1}{2}H_2O$.

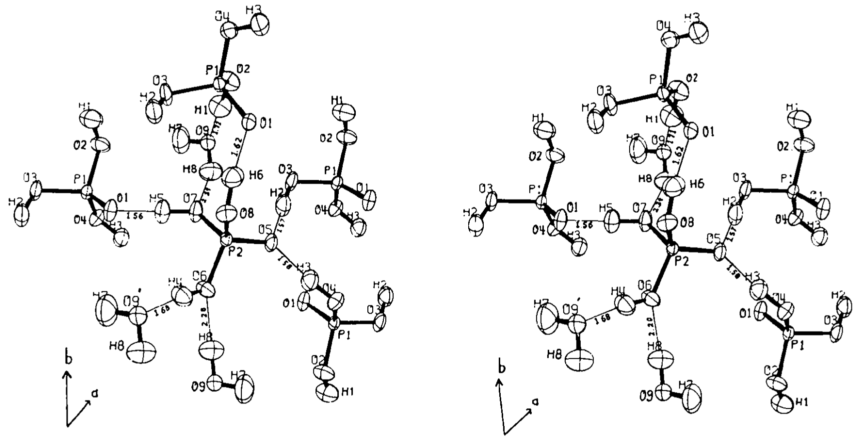

Fig. 3. The environment of the $H_3P(2)O_4$ molecule in $H_3PO_4.\frac{1}{2}H_2O$.

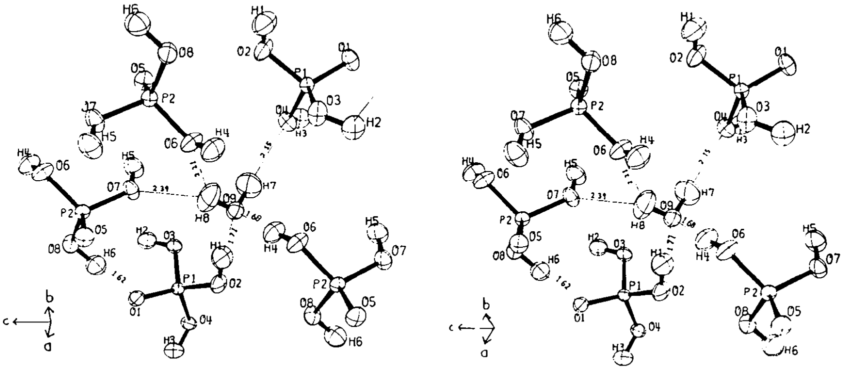

Fig. 4. The environment of the water molecule in $H_3PO_4.\frac{1}{2}H_2O$.

donor in hydrogen bonds to two other neighboring $H_3P(1)O_4$ and $H_3P(2)O_4$ molecules. Atom H(8) of the water molecule may enter into bifurcated hydrogen bonding but the weaker hydrogen bond is very weak as judged by the O(7)···H(8) distance being very near the upper limit of 2·4 Å usually proposed for hydrogen bonding. The hydrogen bonds from the H_2O molecule to the H_3PO_4 molecules are definitely non-linear. The four hydrogens about O(9), two covalently bonded to O(9) and two hydrogen bonded, are arranged approximately in tetrahedral directions about O(9). This suggests that the arrangement of the hydrogens about O(9) results mainly from H···H repulsions and that the possible bifurcation of H(8) is probably a concomitant feature. Significant H···H interactions are indicated by the shortest intermolecular H···H distances in $H_3PO_4.\frac{1}{2}H_2O$: H(4)···H(8) = 2·161 (3) Å; H(4)···H(7) = 2·187 (3) Å; H(1)···H(8) = 2·257 (3) Å and H(1)···H(7) = 2·290 (3) Å. These distances are essentially the same as the H···H distances in $Ca(OH)_2$ (Busing & Levy, 1957), where H···H van der Waals bonding was invoked.

The riding-model corrections (Table 2) are barely significant for the H_3PO_4 molecules but are appreciable for the water molecule. The individual thermal parameters are all fairly large, as is expected for a material within 10 °C of its melting point. However, for once, the model of isotropic secondary extinction was satisfactory in our use of neutron data and the final R_w index is within the limit of the experimental data.

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