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Hydrogen Bonding in the Crystalline State. Structure of $NaH_2PO_4.H_2O$ (Orthorhombic Phase), and Crystal Chemistry of the $NaH_2PO_4.nH_2O$ Series

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$NaH_2PO_4.H_2O$, orthorhombic phase, crystallizes in space group $Pna2_1$, with $a=7{\cdot}616$ (5), $b=7{\cdot}899$ (3), $c=7{\cdot}382$ (2) Å, $Z=4$. The structure was solved (direct methods) and refined anisotropically (least squares, $R=0{\cdot}034$) with 678 reflexions measured on a diffractometer with Mo $K\alpha$ radiation. H atoms were located on difference maps, but were not refined. *Pnam* pseudo-symmetry explains the formation of (001) twins by merohedry. [001] chains of Na coordination octahedra sharing edges develop in pseudo-tetragonal channels present in the framework of P tetrahedra; these are tied by medium-strength acidic hydrogen bonds. Water hydrogen bonds are weak. Bond-strength/bond-length correlations are discussed. Chains of Na polyhedra are present in all structures of the series $NaH_2PO_4.nH_2O$; their linking accounts for the decreasing packing density with increasing hydration. The close similarity of structures of the bihydrated and of the two monohydrated forms is analysed, and a mechanism is proposed for the solid-state reaction $NaH_2PO_4.2H_2O \rightleftarrows NaH_2PO_4.H_2O+H_2O$.

Introduction

The following solid phases are reported (Pascal, 1966) in the system NaH_2PO_4–H_2O between 0 and 100°C: NaH_2PO_4, two phases of $NaH_2PO_4.H_2O$, and $NaH_2PO_4.2H_2O$; in addition, $NaH_2PO_4.4H_2O$ seems to have been obtained at -20°C.

Structural studies of NaH_2PO_4 (Catti & Ferraris, 1974) and of $NaH_2PO_4.2H_2O$ [X-ray and neutron diffraction (Bartl, Catti & Ferraris, 1976)] have appeared. Both phases of $NaH_2PO_4.H_2O$ are reported to be orthorhombic (Pascal, 1966); the rarer was only occasionally obtained (Mitscherlich, 1822; Dufet, 1887) and was said to be isostructural ($a{:}b{:}c=0{\cdot}8170{:}1{:}0{\cdot}4998$) with one of two phases of $NaH_2AsO_4.H_2O$. The latter, however, proved to be monoclinic, pseudo-orthorhombic, in a recent X-ray and neutron-diffraction study (Ferraris, Jones & Sowden, 1974) and, therefore, the corresponding phosphate will be supposed to be monoclinic.

The present work on the more common phase of $NaH_2PO_4.H_2O$ should complete the study of the system and allow a comparison of the different structures, with particular stress on the role of water molecules in a series of crystal hydrates.

Experimental

Crystal data

For experimental measurements the commercial product was used; crystals ({011} prismatic and [100] elongated) are stable at room temperature. Weissenberg photographs and single-crystal diffractometry confirmed the unit cell found by de Wolff and quoted by Pascal (1966). On the basis of systematic absences and of statistical tests with *MULTAN* (Germain, Main & Woolfson, 1971) the non-centrosymmetric space group $Pna2_1$ (No. 33) was chosen instead of *Pnam* (No. 62); the *mm*2 symmetry had already been proposed from morphological studies (where x is interchanged with z) (Dufet, 1887).

Least-squares refinement of 21 θ values measured on a diffractometer [λ(Mo $K\alpha$)$=0{\cdot}71069$ Å] gave $a=7{\cdot}616$ (5), $b=7{\cdot}899$ (3), $c=7{\cdot}382$ (2) Å. Other data are: $M=137{\cdot}998$, $V=441{\cdot}1$ Å^3, $D_m=2{\cdot}055$ (Pascal, 1966), $D_c=2{\cdot}064$ g cm^{-3}, $Z=4$, $F(000)=280$, μ(Mo $K\alpha$)$=6{\cdot}4$ cm^{-1}.

Twinning and intensity measurements

Preliminary measurements on the diffractometer and a careful examination of Weissenberg photographs showed that most crystals had double *hkl* reflexions (but single *hk*0) with the same θ value (on the diffractometer, reflexions appeared double for ω scan but single for θ–2θ scan). Structural considerations, which will be discussed later, support the formation of (001) twins by merohedry; yet, since such twins require a perfect superposition of the reciprocal lattices of the crystals, some kind of macroscopic perturbation must be admitted to account for double reflexions. A crystal with no doubling of reflexions was found and used for intensity measurements: it does not matter whether it was a single crystal or a perfect twin, since Catti & Ferraris (1976) have shown that a crystal structure can be solved without recognizing twinning, if the Laue symmetry of the twin and of the crystal are the same.

The intensities were collected on a Philips PW1100 diffractometer, and the crystal ($0{\cdot}34\times0{\cdot}27\times0{\cdot}21$ mm) had its z axis approximately along the φ axis of the instrument. The measurement conditions were: monochromatized Mo $K\alpha$ radiation, $\theta\le30°$, ω scan, $\Delta\omega=1{\cdot}2°$, scanning speed $0{\cdot}04°$ s^{-1}, background time$=$

(scan time/2) $(I_{\text{bkg}}/I_{\text{peak}})^{1/2}$, attenuating filter inserted for intensites higher than 32000 counts s^{-1}, three reference reflexions. After removal of 94 systematically absent reflexions and 19 with $|F_o| \le 3\sigma(|F_o|)$, 678 independent reflexions remained.

Solution and refinement of the structure

Direct methods (Germain, Main & Woolfson, 1971) allowed a ready solution of the structure by revealing all atoms except H; during the least-squares refinement the origin along z was fixed by the P atom. After isotropic refinement ($R=0{\cdot}07$) the two acidic H atoms were found in a difference map; H(3) was located during the anisotropic refinement, and H(4) only after a correction for secondary extinction by least-squares fitting of the function $I_c/I_o=k(1+gI_c)$ with $k=1{\cdot}028$ and $g=39{\cdot}10^{-7}\ \text{e}^{-2}$. Since positional and thermal parameters of the H atoms were not refinable satisfactorily, in the final calculation of F_c* the coordinates from difference maps and a thermal factor 4 Å^2 (Table 1) were used.

During the last stage of refinement the weighting scheme was $(0{\cdot}12 \le w \le 1)$: $w=1/(1{\cdot}113-0{\cdot}032|F_o|+0{\cdot}0023|F_o|^2)$; a satisfactorily constant value of $w\Delta^2$ averaged over groups (*vs* $|F_o|$ and $\sin\theta$) of reflexions was obtained, except for the group with highest $|F_o|$ and that with lowest $\sin\theta$ values. The final values of R, R_w and of the standard error of an observation of unit weight were 0·034, 0·045 and 0·13, respectively.

Scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1962). The programs of X-RAY System (Stewart, Kundell & Baldwin, 1970) were extensively used.

Discussion

Pseudo-symmetry

By an appropriate choice of origin along z (Table 1) it appears that the general positions occupied by P and Na simulate very closely the special positions 4(c) and 4(a), respectively, of *Pnam*; to a worse approximation, O(1) and W lie on positions 4(c) of the same space group. Such pseudo-symmetry justifies (001) twinning by merohedry from a structural point of view. Further the similarity of a and b can be related to a rough tetragonal pseudo-symmetry in $P4_2$, where Na would occupy 2(b) and 2(a) positions, and x and y of P would be consistent with 4(d) positions.

Description of the structure

The crystal structure contains [001] chains built up by distorted Na octahedra sharing two edges*

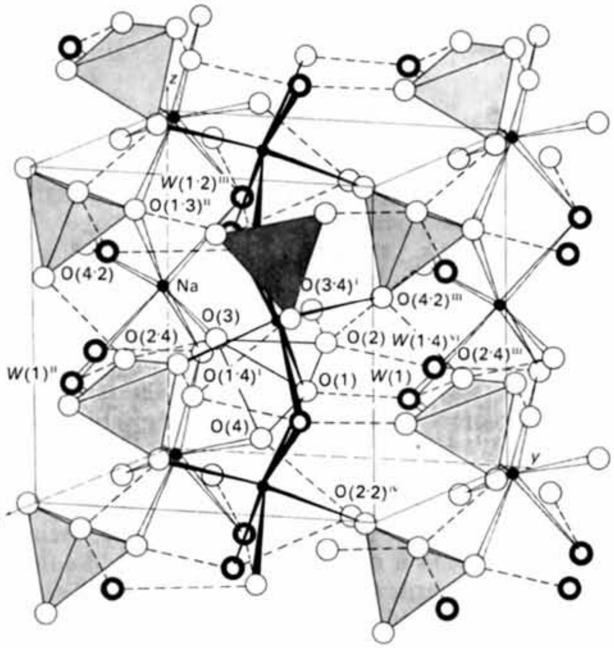

Fig. 1. Clinographic projections down x of the unit cell of $NaH_2PO_4.H_2O$ (orthorhombic phase). Hydrogen bonds are shown by dashed lines.

Table 1. *Fractional atomic coordinates and B_{ij} coefficients* (Å^2) *of the expression* $\exp\left(-\frac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3}B_{ij}h_ih_ja_i^*a_j^*\right)$ *with significant figures of the e.s.d.'s in parentheses*

	x	y	z	B_{11} (or B)	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
P	0·1262 (1)	0·3732 (1)	0·2500	0·78 (2)	0·80 (2)	1·10 (3)	−0·04 (2)	0·06 (3)	−0·01 (3)
Na	−0·0007 (3)	−0·0179 (2)	0·4857 (3)	1·69 (5)	1·48 (5)	1·76 (6)	−0·15 (5)	0·05 (5)	0·23 (5)
O(1)	0·2817 (3)	0·4887 (3)	0·2389 (5)	1·20 (8)	1·40 (8)	2·12 (10)	−0·53 (7)	−0·06 (11)	0·02 (10)
O(2)	−0·0373 (3)	0·4497 (3)	0·3346 (5)	1·14 (9)	1·57 (9)	2·44 (12)	0·15 (7)	0·17 (9)	−0·64 (10)
O(3)	0·1662 (3)	0·2070 (3)	0·3602 (4)	1·31 (8)	1·49 (10)	2·06 (11)	0·07 (7)	0·08 (9)	0·60 (9)
O(4)	0·0744 (4)	0·3009 (3)	0·0580 (4)	2·48 (11)	1·35 (9)	1·30 (9)	−0·33 (9)	−0·24 (9)	−0·13 (8)
W(1)	0·1630 (4)	0·8492 (4)	0·2129 (5)	2·04 (11)	1·86 (10)	2·58 (15)	0·14 (8)	−0·16 (10)	−0·26 (10)
H(1)	0·255	0·170	0·320	4·0					
H(2)	0·050	0·365	−0·040	4·0					
H(3)	0·185	0·750	0·210	4·0					
H(4)	0·270	0·880	0·230	4·0					

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* A list of $|F_o|$ and F_c has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31196 (5 pp.). Copies may be obtained from The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

* A single figure in parentheses denotes an atom of the asymmetric unit; a second figure, ranging from 2 to 4, is included for atoms in the positions $\bar{x},\bar{y},\frac{1}{2}+z$; $\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}+z$; $\frac{1}{2}+x,\frac{1}{2}-y,z$. Roman numerals represent the translations: (I) $-\mathbf{a}$; (II) $-\mathbf{b}$; (III) $+\mathbf{b}$; (IV) $+\mathbf{b}-\mathbf{c}$; (V) $-\mathbf{c}$; (VI) $-\mathbf{a}+\mathbf{b}$.

[$W(1)^{\mathrm{II}}\cdots\mathrm{O}(1,4)^{\mathrm{I}}$ and $W(1,2)^{\mathrm{III}}\cdots\mathrm{O}(1,3)^{\mathrm{II}}=3{\cdot}180$ Å]; these are related by the 2_1 operation and are much shorter than the others because of repulsion between the Na^+ ions. The whole chain is stretched along z (Fig. 1): the two shared edges (which are roughly perpendicular to z) subtend angles markedly smaller than 90°, and the two edges of the octahedron which are parallel to z [$W(1)^{\mathrm{II}}\cdots\mathrm{O}(1,3)^{\mathrm{II}}$ and $W(1,2)^{\mathrm{III}}\cdots\mathrm{O}(1,4)^{\mathrm{I}}$ $=4{\cdot}059$ Å] are long and subtend angles greater than 90°. The chains are evenly distributed in space because of the quasi-symmetry $P4_2$ obeyed by Na atoms; contiguous chains are directly linked by the weak hydrogen bond $W(1)$–H(3)$\cdots$O(1).

Table 2. *Interatomic distances and* O$\cdots$Na$\cdots$O *angles in the* Na *coordination polyhedron*

The e.s.d.'s are 0·004 Å for the distances and 0·2° for the angles.

Na–O(1,3)$^{\mathrm{II}}$	2·506 Å	Na–O(4,2)	2·366 Å
Na–O(1,4)$^{\mathrm{I}}$	2·474	Na–$W(1)^{\mathrm{II}}$	2·591
Na–O(3)	2·373	Na–$W(1,2)^{\mathrm{III}}$	2·474
Average	2·464		

O(1,3)$^{\mathrm{II}}$–O(3)	3·309 Å	85·4°
O(1,3)$^{\mathrm{II}}$–O(4,2)	3·462	90·5
O(1,3)$^{\mathrm{II}}$–$W(1)^{\mathrm{II}}$	4·059	105·5
O(1,3)$^{\mathrm{II}}$–$W(1,2)^{\mathrm{III}}$	3·180	79·4
O(1,4)$^{\mathrm{I}}$–O(3)	3·431	90·1
O(1,4)$^{\mathrm{I}}$–O(4,2)	3·583	95·5
O(1,4)$^{\mathrm{I}}$–$W(1)^{\mathrm{II}}$	3·180	79·4
O(1,4)$^{\mathrm{I}}$–$W(1,2)^{\mathrm{III}}$	4·059	105·5
O(3)—$W(1)^{\mathrm{II}}$	3·029	75·1
O(3)—$W(1,2)^{\mathrm{III}}$	3·642	97·4
O(4,2)—$W(1)^{\mathrm{II}}$	3·342	84·6
O(4,2)—$W(1,2)^{\mathrm{III}}$	3·807	103·7
O(1,3)$^{\mathrm{II}}$–O(1,4)$^{\mathrm{I}}$	–	173·4
$W(1)^{\mathrm{II}}$—$W(1,2)^{\mathrm{III}}$	–	170·4
O(3)—O(4,2)	–	157·3

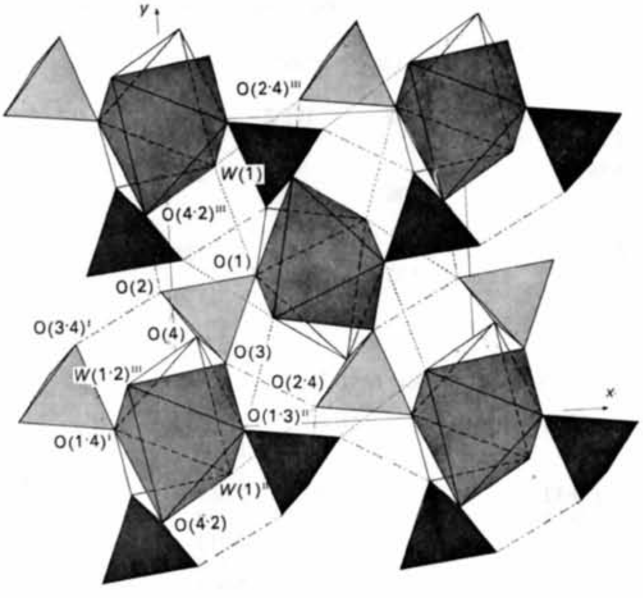

Fig. 2. Projection of the unit cell of $\mathrm{NaH_2PO_4.H_2O}$ (orthorhombic phase) onto the (001) plane. Dashed–dotted and dotted lines show acidic and water hydrogen bonds, respectively.

A framework of P tetrahedra (Table 3) is formed by two systems of [100] and [001] chains where the acidic hydrogen bonds (Table 4) O(3)–H(1)$\cdots$O(2,4) and O(4)–H(2)$\cdots$O(2,2)$^{\mathrm{IV}}$ supply the respective linkages. This framework shows [001] pseudo-tetragonal channels around the Na octahedra (Fig. 2).

Table 3. *Interatomic distances, uncorrected* (*A*) *and corrected* (*B*) *for thermal motion* (*riding model*), *and* O–P–O *angles for the* P *tetrahedron*

The e.s.d.'s are 0·003 and 0·004 Å for P–O and O$\cdots$O distances, respectively, and 0·2° for the angles.

	A	*B*
P–O(1)	1·498 Å	1·507 Å
P–O(2)	1·519	1·529
P–O(3)	1·575	1·583
P–O(4)	1·579	1·589
Average	1·543	1·552
	Distances	Angles
O(1)$\cdots$O(2)	2·549 Å	115·4°
O(1)$\cdots$O(3)	2·555	112·5
O(1)$\cdots$O(4)	2·545	111·7
O(2)$\cdots$O(3)	2·473	106·1
O(2)$\cdots$O(4)	2·505	108·0
O(3)$\cdots$O(4)	2·453	102·3
Average	2·514	109·3

Looking at the structure from another side, $(1\bar{1}0)$ planes containing alternate Na and P atoms can be recognized. Table 6 lists the root-mean-square thermal displacements.

Configuration of groups with hydrogen bonds

The water molecule forms two very weak hydrogen bonds (Table 4) and the stability of the hydrate at room temperature should then be ascribed to $\mathrm{H_2O}$ coordinating two Na^+ ions. $W(1)$ is of class 2, type *A* (Ferraris & Franchini-Angela, 1972) and, in spite of the weakness of hydrogen bonds, it shows fairly regular tetrahedral surroundings: $\angle$Na–W–Na is 94° and the angle between the planes Na–W–Na and O$\cdots W\cdots$O is 85°. $W(1)$ has three other O$\cdots$O contacts slightly longer than 3 Å, two of which are edges of the Na octahedron (Table 2); the third contact is $W(1)\cdots$ O(3,3)$^{\mathrm{V}}$ (3·120 Å): O(3,3)$^{\mathrm{V}}$ is nearly equidistant from H(3) and H(5) (2·84 and 2·87 Å, respectively), resembling the situation found in $\mathrm{NaHSO_4.H_2O}$ (Catti, Ferraris & Franchini-Angela, 1975).

The two acidic hydrogen bonds (Table 4) are very similar and are of average strength; their bendings are remarkably high for this kind of bond (but they are determined with low accuracy, of course). Both O(3) and O(4) show an approximately planar trigonal environment (with H, P and Na). O(1) coordinates two Na^+ ions and is the acceptor of a weak hydrogen bond from $W(1)$; O(2) is in an interesting position, since it coordinates no Na and is the acceptor of three hydrogen bonds: its environment is tetrahedral but very distorted.

As already remarked for similar structures (Bartl *et al.*, 1976), by including the H atoms in the F_c calculation the relative O···O distances were lengthened: the highest increase was 0·006 Å for acidic hydrogen bonds.

Empirical bond-length/bond-strength correlations

Bond-strength values calculated by the universal curves $s=(R/R_0)^{-N}$ (Brown & Shannon, 1973) are reported in Table 5. As for hydrogen bonds, the *s vs* O···O distance relationships of Brown (1976) and Donnay & Allmann (1970) were used, because of the low accuracy of H positions. On the whole, the former values (above) give better $\sum s_i$ values for O atoms than the latter (below); however, this structure is a further proof (*cf.* Bartl *et al.*, 1976; Catti *et al.*, 1975) that hydrogen bonds are a weak point of the proposed correlations.

Predictive relationships for the phosphate group (Baur, 1974) have been tested. Distortion indices of 0·035, 0·025 and 0·022 were obtained for O–P–O angles, O···O and P–O distances, respectively; these values should be compared with the average values given by Baur for acidic orthophosphates: 0·025, 0·011 and 0·017. The geometrical correlations proposed by the same author led to values of 1·536 and 2·506 Å for $(\text{P–O})_{\text{mean}}$ and $(\text{O}\cdots\text{O})_{\text{mean}}$, respectively. The results are less satisfactory for individual O–P–O angles, where the relationships *vs* the P–O distance are more reliable than those *vs* the O···O distance, on the whole; the same situation was found for $NaH_2PO_4.2H_2O$ (Bartl *et al.*, 1976).

Table 6. *Parameters characterizing the principal directions of thermal vibration for* P, Na, *and* O *atoms: root-mean-square displacements A and angles which the principal directions make with x(B), y(C) and z(D)*

	A	*B*	*C*	*D*
P	0·102 Å	126°	37°	81°
	0·119	79	94	11
	0·097	38	53	96
Na	0·149	25	103	69
	0·155	101	58	34
	0·128	68	35	116
O(1)	0·15	128	40	100
	0·16	98	83	10
	0·10	39	51	88
O(2)	0·13	51	45	71
	0·19	87	117	27
	0·11	39	123	109
O(3)	0·13	6	90	96
	0·18	85	58	33
	0·12	94	32	122
O(4)	0·14	86	45	135
	0·18	16	104	99
	0·12	74	48	46
W(1)	0·16	24	78	69
	0·19	106	109	25
	0·15	108	23	77

Table 4. *Interatomic distances* (Å) *and angles* (°) *in the hydrogen bonds*

A prime is intended for an atom on the second line for each donor atom. The e.s.d.'s are 0·004 Å for the distances and 0·2° for the angles.

A	*B*	*C*	*AB*	*BC*	*AC*	*BB′*	*BAB′*	*CAC′*	*ABC*
W(1)	H(3)	O(1)	0·80	2·20	2·994	1·22	95	105·2	170
	H(4)	$O(2,4)^{III}$	0·86	2·14	2·923				152
O(3)	H(1)	O(2,4)	0·80	1·85	2·583		106		154
	P(1)								
O(4)	H(2)	$O(2,2)^{IV}$	0·90	1·74	2·585		125		156
	P(1)								

Table 5. *Bond-strength balance; for explanation see text*

	P	Na	H(1)	H(2)	H(3)	H(4)	$\sum s_i$
O(1)	1·411	0·155 0·163			0·08 0·13		1·809 1·859
O(2)	1·329		0·32 0·17	0·32 0·17		0·10 0·11	2·069 1·779
O(3)	1·138	0·195	0·68 0·83				2·013 2·163
O(4)	1·125	0·198		0·68 0·83			2·003 2·153
W(1)		0·134 0·163			0·92 0·87	0·90 0·89	2·117 2·057
$\sum s_i$	5·003	1·008	1·00	1·00	1·00	1·00	

Discussion of the structures of the $NaH_2PO_4.nH_2O$ *series*

The packing density of the crystalline phases NaH_2PO_4, $NaH_2PO_4.H_2O$ (orthorhombic) and $NaH_2PO_4.2H_2O$ decreases with increasing hydration as shown by the calculated densities (2·371, 2·064 and 1·894 g cm^{-3}, respectively);* an analogous behaviour was observed in the series $CaHAsO_4.nH_2O$ with $0 \leq n \leq 3$ (Catti & Ferraris, 1973). The variation of packing density in the series $NaH_2PO_4.nH_2O$ can be related to a different linkage in chains of Na polyhedra. Such chains are parallel to x in NaH_2PO_4, and to z in all the other compounds, including $NaH_2PO_4.H_2O(m)$; the corresponding translation vectors always comprise two Na polyhedra, and their lengths are a measure of the bending of the chains themselves: 5·166 Å in the monohydrated (m) arsenate, 6·606 Å in the bihydrated, 6·808 Å in the anhydrous, and 7·382 Å in the monohydrated (o) phosphate. In NaH_2PO_4 we have pairs of centrosymmetrical chains linked by sharing edges of polyhedra; in the two phases (o) and (m) of $NaH_2PO_4.H_2O$ we find straight single chains with polyhedra sharing two edges, and very bent single chains with polyhedra sharing two vertices, respectively; in $NaH_2PO_4.2H_2O$ bent single chains are present, where the Na polyhedra share two vertices. Clearly, the bending of chains and the sharing of more elements in and between the chains have the same effect: an increase of packing density parallel to the loss of water and to the decrease of the stoichiometric ratio O/Na.

A close structural similarity can be observed between the bihydrated and the two monohydrated phases. In these compounds a framework of P tetrahedra is formed by two systems of bent chains parallel to x and z, respectively; in each chain the tetrahedra are linked by one of the two independent acidic hydrogen bonds. [001] channels, where the Na chains are lodged, are present in the framework. The channels look pseudo-hexagonal in $NaH_2PO_4.2H_2O$, and pseudo-tetragonal in $NaH_2PO_4.H_2O(o)$; in the (m) monohydrated phase, they have a rough hexagonal aspect.

On the basis of the crystal structures, a mechanism can be proposed for the (questionably reversible, *cf.* below) solid-state reaction $NaH_2PO_4.2H_2O \rightleftarrows NaH_2PO_4.H_2O+H_2O$. Transition to the ($o$) monohydrated phase: all the Na polyhedra lose their $W(2)$ and link by that vertex, so that now they share a whole edge; the hexagonal channels of tetrahedra shrink to quadrangular ones. Transition to the (m) monohydrated phase: this should be even easier; the vertex of the Na polyhedron which is set free by the loss of $W(2)$ links to a P tetrahedron by O(2) which was not Na coordinated. Actually the latter reaction should be much faster in the opposite direction, in order to account for the reported low stability of $NaH_2PO_4.H_2O(m)$; the former transition, instead, should be faster in the direction of dehydration, since the bihydrate transforms at room temperature into the orthorhombic monohydrate, as confirmed by X-ray examination of the product.

As for $NaH_2PO_4.2H_2O$ and $NaH_2PO_4.H_2O(o)$, we would add that the order of stability, which we have observed, is the opposite of that reported in the literature (*cf.* Pascal, 1966); Dufet (1887) noticed that the introduction of the bihydrate in his laboratory affected the stability of the monohydrate (which was introduced in our laboratory after the bihydrate). These observations could be related to similar phenomena reported by Woodard & McCrone (1975).

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* The density of $NaH_2PO_4.H_2O(m)$ should also be intermediate between that of the anhydrous and of the bihydrated form, according to the behaviour of the corresponding arsenates.

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