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The Crystal Structure of $Na_2HPO_4.2H_2O$. Competition between Coordination and Hydrogen Bonds

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$Na_2HPO_4.2H_2O$ crystallizes in space group *Pbca* with a = 16·872 (9), b = 10·359 (4), c = 6·599 (3) Å, Z = 8. The structure was refined to R = 0·036 for 1268 counter reflexions. H atoms were refined isotropically. Competition between stronger but non-directional coordination bonds and weaker but substantially directional hydrogen bonds explains the distortions of the two independent Na coordination polyhedra; the inclusion in these polyhedra of O atoms at 3·146 (CN 5 + 1) and 3·184 Å (CN 6 + 1) is discussed in terms of geometrical environment and bond-strength/bond-length correlations.

Introduction

Members with n = 0, 2, 7, 12 are known in the series $Na_2HPO_4.nH_2O$, and two different phases (α and β) are known for the dodecahydrate (Pascal, 1966). The structure of the heptahydrate was described by Baur & Khan (1970), together with that of the isostructural arsenate (Ferraris & Chiari, 1970; Ferraris, Jones & Yerkess, 1971). As part of an investigation of hydrogen bonding, particularly in hydrates (Catti & Ferraris, 1973, 1976), the results of the structural study of $Na_2HPO_4.2H_2O$ are reported here; the structure determination of β-$Na_2HPO_4.12H_2O$ is in progress.

Experimental

Weissenberg photographs and single-crystal diffractometry confirmed the orthorhombic unit cell (Pascal, 1966; a and b interchanged); the space group *Pbca* was determined from systematic absences. The cell reported by Zsoldos (1962) can be obtained by the transformation 010/002/100, but it shows some inconsistencies with the calculated interplanar spacings reported for comparison with the corresponding powder spectrum.

Least-squares refinement of 22 θ values measured on a diffractometer [λ(Mo $K\alpha$) = 0·71069 Å] yielded a = 16·872 (9), b = 10·359 (4), c = 6·599 (3) Å. Other crystal data are: V = 1153·4 Å^3, M_r = 177·997, D_m = 2·066 (Pascal, 1966), D_c = 2·050 g cm^{-3}, Z = 8, F(000) = 720, μ(Mo $K\alpha$) = 6·0 cm^{-1}.

Intensities were collected on a Philips PW 1100 automatic four-circle diffractometer from a tabular fragment (0·30 × 0·22 × 0·08 mm) with an approximately triangular shape (commercial product). The measurement conditions were: Mo $K\alpha$ radiation, graphite monochromator, $\theta \leq 30°$, ω scan, $\Delta\omega = 1°$, scanning speed = 0·05° s^{-1}, background time = (scan time/2)$(I_{\rm bkg}/I_{\rm pk})^{1/2}$, attenuating filter inserted for intensities higher than 32 000 counts s^{-1}, three reference reflexions. After removing 417 reflexions with $|F_o| \leq 3\sigma(|F_o|)$, 1268 independent observations were left; 17 of these were later excluded from the refinement because of suspected extinction.*

Solution and refinement of the structure

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971); all the non-hydrogen atoms

Table 1. *Fractional atomic coordinates with significant figures of the e.s.d.'s in parentheses*

	x	y	z
P	0·66256 (3)	0·48293 (5)	0·62163 (9)
Na(1)	0·77105 (6)	0·23198 (10)	0·82964 (15)
Na(2)	1·00021 (6)	0·14973 (10)	0·64229 (16)
O(1)	0·6491 (1)	0·5210 (2)	0·8438 (3)
O(2)	0·6937 (1)	0·3463 (2)	0·5998 (3)
O(3)	0·5903 (1)	0·5103 (2)	0·4941 (3)
O(4)	0·7320 (1)	0·5792 (2)	0·5489 (3)
W(1)	0·5676 (1)	0·1837 (2)	0·5504 (3)
W(2)	0·8958 (1)	0·3206 (2)	0·6820 (3)
H(1)	0·586 (2)	0·115 (3)	0·491 (5)
H(2)	0·605 (3)	0·230 (5)	0·553 (8)
H(3)	0·901 (2)	0·381 (4)	0·778 (7)
H(4)	0·889 (3)	0·373 (4)	0·566 (7)
H(5)	0·772 (2)	0·536 (4)	0·479 (6)

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32697 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

were revealed, except for Na(2),* which appeared on a subsequent difference map. After a least-squares anisotropic cycle, a difference map showed all the H atoms; these were then refined isotropically. An analysis of secondary extinction by the least-squares fitting of the function $I_c/I_o = k(1 + gI_c)$ was unsuccessful, because the ratio I_c/I_o for groups of reflexions *vs* I_o turned out to be close to 1, except for about a hundred weak reflexions (which systematically showed $|F_c| < |F_o|$).†

The full-matrix least-squares refinement converged to $R = 0{\cdot}036$ (standard error of an observation: 1·50); unitary weights were used, since the average values of Δ^2 for groups of reflexions *vs* $|F_o|$ and $\sin\theta$ were satisfactorily constant. The final atomic parameters are listed in Table 1. Scattering factors for neutral atoms (*International Tables for X-ray Crystallography*, 1962) and the XRAY system (Stewart, Kundell & Baldwin, 1970) were used.

Discussion

Description of the structure

Owing to the high Na/P stoichiometric ratio, the structure is clearly dominated by the framework of Na coordination polyhedra (Fig. 1, Table 2). (100) layers of Na(2) polyhedra at $x = 0, \frac{1}{2}$ are observed; linking within the layer is by the sharing of two vertices, $W(1,3)^{\text{III}}$ and $W(1,8)^{\text{III}}$ along [001], and the edge $O(3,4)^{\text{I}}$–$O(3,3)^{\text{III}}$. The Na(1) coordination polyhedra share two edges [$O(2)$–$O(4,4)^{\text{I}}$ and $O(2,6)$–$O(4,7)^{\text{II}}$] with one another, forming [001] chains at about $x = \frac{1}{4}$, $y = \frac{1}{4}$, half-way between the above layers; such chains are connected to the Na(2) polyhedra of the layers by sharing the $W(2)$ vertex. If $W(2,6)$ and $O(1,4)^{\text{I}}$ are included in the coordination spheres of Na(1) and Na(2) (Table 2), respectively, then the Na(1) polyhedra share faces with one another and edges with the Na(2) polyhedra.

Between the chains of Na(1) polyhedra, at about $y = 0, \frac{1}{2}$, [001] bent chains of P tetrahedra (Table 3) linked by the acidic hydrogen bond are present; further linking within each chain is provided by the hydrogen bonds of $W(2)$ which connect P tetrahedra equivalent by a c translation, so as to bridge the bends. Adjacent chains are tied by the hydrogen bonds donated by $W(1)$. All the anionic O atoms are also vertices of one or two Na polyhedra and, in particular, the O(1)–O(4) edge is shared with a Na(1) polyhedron.

Since Na(1) and Na(2) chiefly coordinate anionic and water O atoms, respectively, the structure can also

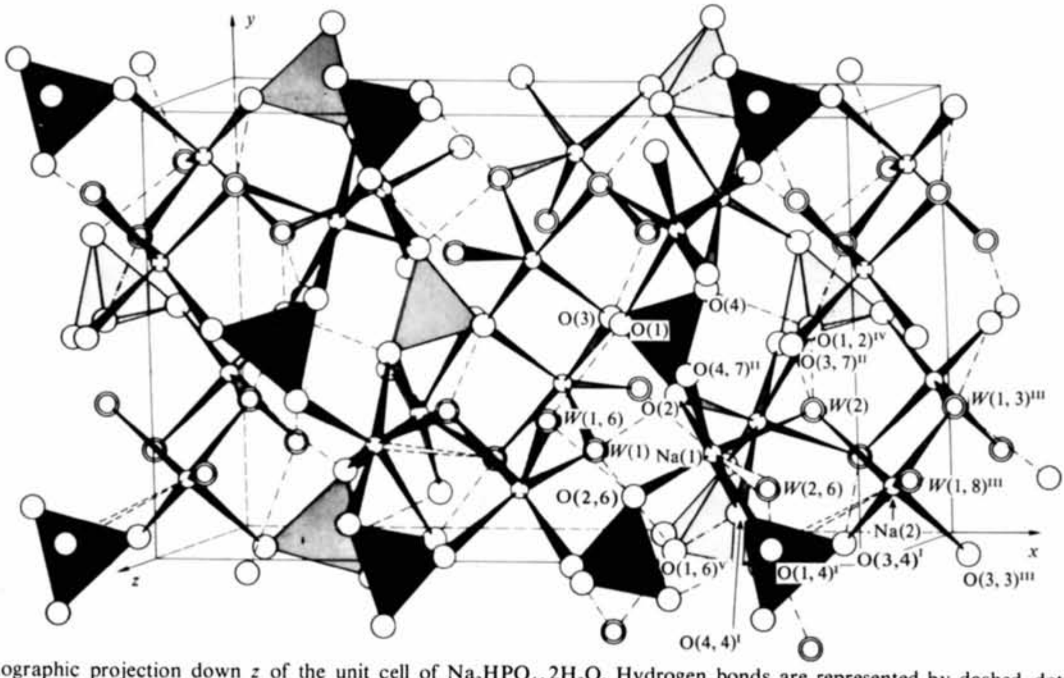

Fig. 1. Clinographic projection down z of the unit cell of $Na_2HPO_4.2H_2O$. Hydrogen bonds are represented by dashed–dotted lines; dashed rods show a few cases of the longest Na–O coordination bonds (see text).

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* A single figure in parentheses denotes an atom of the asymmetric unit; a second figure, ranging from 2 to 8, is included for atoms in the positions $(\bar{x},\bar{y},\bar{z})$, $\pm(\frac{1}{2}+x, \frac{1}{2}-y, \bar{z})$, $\pm(\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z)$ and $\pm(\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z)$. Roman numerals represent the following translations: (I) $+\mathbf{a}-\mathbf{b}$; (II) $+\mathbf{a}+\mathbf{b}$; (III) $+\mathbf{c}$; (IV) $+\mathbf{a}+\mathbf{b}-\mathbf{c}$; (V) $-\mathbf{c}$; (VI) $+\mathbf{a}$.

† This effect has been observed in all the structures studied in this Institute. Several factors may account for it: (i) the presence of multiple scattering, which causes a higher percentage increase of $|F_o|$ for weak reflexions; (ii) an underestimate of the background, again with larger percentage errors for weak reflexions; (iii) strong intensities are underestimated because of primary and secondary extinction and absorption effects (the latter is higher at low angles and thus for most of the largest $|F_o|$'s), so that the scale factor is overestimated.

be viewed as a series of (100) layers containing Na(2) atoms and water molecules openly packed, and these sandwich layers of Na(1), P and O atoms which are much more densely packed.

Table 2. *Interatomic distances and* O···Na···O *angles in the* Na *coordination polyhedra*

For the e.s.d.'s see Table 3.

Na(1)–O(1,4)$^{\mathrm{I}}$	2·569 Å	Na(2)–O(3,3)$^{\mathrm{III}}$	2·423 Å
Na(1)–O(2)	2·326	Na(2)–O(3,4)$^{\mathrm{I}}$	2·318
Na(1)–O(2,6)	2·354	Na(2)–*W*(1,3)$^{\mathrm{III}}$	2·427
Na(1)–O(4,4)$^{\mathrm{I}}$	2·438	Na(2)–*W*(2)	2·511
Na(1)–O(4,7)$^{\mathrm{II}}$	2·434	Na(2)–*W*(1,8)$^{\mathrm{III}}$	2·352
Na(1)–*W*(2)	2·495	Average	2·406
Average	2·436	Na(2)–O(1,4)$^{\mathrm{I}}$	3·146
Na(1)–*W*(2,6)	3·184	Average	2·530
Average	2·543		

O(2)–*W*(2)	3·464 Å	91·8°
O(2)–O(4,4)$^{\mathrm{I}}$	3·057	79·8
O(2)–O(2,6)	3·856	111·0
O(2)–O(4,7)$^{\mathrm{II}}$	3·310	88·1
O(4,7)$^{\mathrm{II}}$–*W*(2)	3·405	87·4
O(4,7)$^{\mathrm{II}}$–O(2,6)	3·057	79·3
O(4,4)$^{\mathrm{I}}$–*W*(2)	3·418	87·7
O(4,4)$^{\mathrm{I}}$–O(2,6)	3·923	109·9
O(1,4)$^{\mathrm{I}}$–*W*(2)	3·369	83·4
O(1,4)$^{\mathrm{I}}$–O(4,4)$^{\mathrm{I}}$	2·471	59·1
O(1,4)$^{\mathrm{I}}$–O(4,7)$^{\mathrm{II}}$	4·576	132·3
O(1,4)$^{\mathrm{I}}$–O(2,6)	3·433	88·3
W(2,6)–O(1,4)$^{\mathrm{I}}$	2·873	58·7
W(2,6)–*W*(2)	3·610	77·9
W(2,6)–O(2,6)	3·464	75·8
W(2,6)–O(4,7)	3·418	73·6
O(4,7)$^{\mathrm{II}}$–O(4,4)$^{\mathrm{I}}$	–	166·8
O(2,6)–*W*(2)	–	153·0
W(1,8)$^{\mathrm{III}}$–*W*(2)	3·679	98·3
W(1,8)$^{\mathrm{III}}$–*W*(1,3)	3·574	96·8
W(1,8)$^{\mathrm{III}}$–O(3,3)$^{\mathrm{III}}$	3·572	96·9
W(1,8)$^{\mathrm{III}}$–O(3,4)$^{\mathrm{I}}$	4·400	140·9
W(2)–O(3,4)$^{\mathrm{I}}$	3·454	91·3
W(2)–*W*(1,3)	3·280	83·2
W(2)–O(3,3)$^{\mathrm{III}}$	4·885	164·0
O(3,3)$^{\mathrm{III}}$–O(3,4)$^{\mathrm{I}}$	3·055	80·2
O(3,3)$^{\mathrm{III}}$–*W*(1,3)	3·426	89·9
O(3,4)$^{\mathrm{I}}$–*W*(1,3)	4·151	122·0
O(1,4)$^{\mathrm{I}}$–*W*(1,8)$^{\mathrm{III}}$	4·087	95·0
O(1,4)$^{\mathrm{I}}$–*W*(2)	3·369	72·1
O(1,4)$^{\mathrm{I}}$–O(3,4)$^{\mathrm{I}}$	2·515	52·2
O(1,4)$^{\mathrm{I}}$–O(3,3)$^{\mathrm{III}}$	4·625	111·7

Hydrogen bonding and the coordination polyhedra

All the hydrogen bonds show regular geometrical features (Table 4), taking into account the low accuracy of the H atom positions determined by X-ray diffraction. Normal environments are also shown, generally, by donor and acceptor O atoms; the two water molecules *W*(1) and *W*(2) are characterized by fairly regular tetrahedral configurations of class 2, type *A* (Ferraris & Franchini-Angela, 1972), and O(2), O(3), O(4) also show approximately tetrahedral surroundings. A different behaviour is observed for O(1), which, besides the bond with P, accepts three hydrogen bonds (Table 4) and coordinates Na(1). H(1), H(4) and Na(1) are roughly coplanar with O(1), O(1)–H(5) is approximately perpendicular to that plane, and O(1)–P lies slightly below it, so that a very irregular environment is produced with an empty space on the opposite side of H(5). If Na(2,4)$^{\mathrm{VI}}$ (at 3·146 Å) and Na(1,6)$^{\mathrm{V}}$ (at 3·184 Å) are included in the coordination spheres of O(1) and *W*(2), respectively, then (i) O(1) fills the empty coordination site and achieves an octahedral environment which is fairly reasonable geometrically, but is quite unusual for O atoms of oxyanions (since

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 0·002 Å and 0·1° for distances and angles respectively.

	A	*B*
P–O(1)	1·535 Å	1·543 Å
P–O(2)	1·517	1·523
P–O(3)	1·509	1·517
P–O(4)	1·612	1·618
Average	1·543	1·550
	Distances	Angles
O(1)–O(2)	2·537 Å	112·5°
O(1)–O(3)	2·515	111·4
O(1)–O(4)	2·471	103·5
O(2)–O(3)	2·534	113·7
O(2)–O(4)	2·521	107·3
O(3)–O(4)	2·522	107·8
Average	2·517	109·4

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

A prime denotes an atom on the second line for each donor atom.

A	*B*	*C*	*AB*	*BC*	*AC*	*BB′*	*BAB′*	*CAC′*	*ABC*
W(1)	H(1)	O(1,6)$^{\mathrm{V}}$	0·87 (3)	2·02 (3)	2·872 (3)	1·29 (6)	106 (2)	98·0 (1)	168 (3)
	H(2)	O(2)	0·79 (5)	1·95 (5)	2·732 (3)				172 (5)
W(2)	H(3)	O(3,7)$^{\mathrm{II}}$	0·89 (4)	1·83 (4)	2·714 (3)	1·42 (6)	101 (4)	104·1 (1)	174 (4)
	H(4)	O(1,7)$^{\mathrm{IV}}$	0·95 (5)	1·94 (4)	2·873 (3)				167 (4)
O(4)	H(5)	O(1,7)$^{\mathrm{IV}}$	0·93 (4)	1·71 (4)	2·634 (2)		112 (2)		172 (4)
	P(1)		1·612 (2)						

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

	P	Na(1)	Na(2)	H	Σ
O(1)	1·25	0·14	0·06	0·25 0·14 0·14	1·98
O(2)	1·34	0·20 0·21		0·21	1·96
O(3)	1·35		0·18 0·22	0·21	1·96
O(4)	1·03	0·17 0·18		0·75	2·13
W(1)			0·18 0·20	0·79 0·86	2·03
W(2)		0·16 0·06	0·15	0·86 0·79	2·02
Σ	4·97	1·12	0·99	5·00	12·08

they normally show tetrahedral or triangular environments); (ii) *W*(2) becomes class 3, type *O*, but only formally, since Na(1,6)$^{\mathrm{V}}$ is far away from the plane *W*(2)Na(1)Na(2) [the *W*(2)—Na(1,6)$^{\mathrm{V}}$ direction forms an angle of 68° with that plane, and is roughly normal to the intersection of that plane with the plane of the H_2O molecule]. On geometrical grounds, the influence of *W*(2,6) and O(1,4)$^{\mathrm{I}}$ on the Na atoms should not be negligible, since they are placed in front of very open faces of the 'square' bipyramid with vertices O(2) and O(1,4)$^{\mathrm{I}}$, coordinated by Na(1) (CN 6), and of the 'pentagonal' bipyramid with vertex *W*(1,8)$^{\mathrm{III}}$ coordinated by Na(2) (CN 5) respectively. If the bond-strength balance of the structure (Table 5), calculated by Brown & Wu's (1976) formula and parameters and Brown's (1976) curves for hydrogen bonds, is taken into account, a slightly different situation can be observed in the two cases: the bond strength of the Na(2)···O(1,4)$^{\mathrm{I}}$ contact (0·06 v.u.) appears to contribute positively to the sums of both Na(2) and O(1), whereas an equal bond strength given by the Na(1)···*W*(2,6) contact causes a substantial overbonding of Na(1). Besides, the inclusion of *W*(2,6) in the Na(1) coordination polyhedron would cause the hydrogen bridge *W*(2,6)···O(1,4)$^{\mathrm{I}}$ to be an edge of such a polyhedron, so as to achieve a very unlikely configuration (Baur, 1973).

Several cases of irregular coordination of the Na^+ ion can be found in the literature, *e.g.* $Na_2CO_3.H_2O$ (Wu & Brown, 1975), $Na_2Cu(SeO_4)_2.2H_2O$ (Peytavin & Philippot, 1973), NaH_2PO_4 (Catti & Ferraris, 1974) for 6 + 1 coordination, and $(NaPO_3)_x$ (McAdam, Jost & Beagley, 1968) for 5 + 1 coordination. The general reasons for this phenomenon are related to the low stoichiometric ratio O atoms/cations, associated with a high number of H atoms; a competition then occurs between coordination bonds and hydrogen bonds in engaging the available O atoms, so that considerable distortions of the coordination spheres are observed. In this respect, the stronger but non-directional ionic bonds of cations may sometimes act as even more efficient 'strain absorbers' than the weaker but substantially directional hydrogen bonds (Ferraris & Franchini-Angela, 1972) in the crystal structure.

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