full-matrix least-squares refinement. The refinement converged with the final atomic parameter values given in Table 1. The structure is illustrated in Fig. 1 and the interatomic distances and angles are given in Table 2.

Conclusion

The phase IV structure of ammonium nitrate has been confirmed. The phase II structure has been determined and shows orientational disorder of both the ammonium and nitrate ions. The shortest distances of the H atoms to O atoms in phase II are 2·008 (6), 2·658 (4) Å for one relative orientation of the ammonium and nitrate ions, compared with 2·622 (8), 2·130 (3) Å, respectively, for the other relative orientation. As the limit for H···O bonding is ~2·38 Å (Hamilton & Ibers, 1968), this would suggest that the NH_4, and probably the NO_3, ions are in dynamic (as opposed to static) disorder between their two equivalent positions.

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Pseudo-Symmetry and Hydrogen Bonding in the Crystal Structure of $NaH_2PO_2.\frac{4}{5}H_2O$

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Abstract

$NaH_2PO_2.\frac{4}{5}H_2O$ crystallizes in space group $P2_1/n$ with $a = 11{\cdot}127$ (4), $b = 13{\cdot}572$ (4), $c = 12{\cdot}930$ (4) Å, $\beta = 102{\cdot}98$ (8)°, $Z = 20$. The structure was refined to $R = 0{\cdot}043$ for 2684 counter reflexions. H atoms were refined isotropically. All atomic positions are consistent with a strong *C* pseudo-symmetry. The distorted tetrahedral configurations of the $[H_2PO_2]^-$ ions are discussed in terms of atomic repulsion forces. Two very low O···*W*···O′ angles (76·2 and 78·4°) are shown by hydrogen bonds, O···O′ being edges of the Na coordination polyhedra. The Na octahedra form [101] chains by sharing faces and edges; a weak link between chains is provided by sharing vertices (water molecules only) between polyhedra and by hydrogen bonding. On the basis of the structural topology, a dehydration mechanism is proposed.

Introduction

A series of hydrated sodium hydrogenorthophosphates have recently been the subject of structural studies to clarify the relative role of the Na—O coordination bonds and of hydrogen bonding in determining their structural topology and stability *vs* dehydration (*cf.* Catti, Ferraris & Ivaldi, 1978). Since the stoichiometric ratio O/Na and the number of acidic hydrogen atoms are the crucial parameters controlling the condensation of the Na coordination polyhedra (Catti & Ivaldi, 1977), it seemed interesting to change them by substituting the $[PO_2(OH)_2]^-$ or $[PO_3(OH)]^{2-}$ oxyanions by the hypophosphite ion $[H_2PO_2]^-$, where the two hydrogen atoms are not acidic and not involved in hydrogen bonds. The structure of the only known hydrated sodium hypophosphite $NaH_2PO_2.\frac{4}{5}H_2O$ has therefore been examined. This study can also provide

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new data on the structural chemistry of the $[H_2PO_2]^-$ ion. Only one neutron-diffraction study of a hypophosphite has been reported: a primitive study of $Ca(H_2PO_2)_2$ (Loopstra, 1958). Hypophosphites studied with X-rays are: $NH_4H_2PO_2$ (Zachariasen & Mooney, 1934); KH_2PO_2 (Akimoto, 1965); $CaNa(H_2PO_2)_3$ (Matsuzaki & Iitaka, 1969); $Mg(H_2PO_2)_2.6H_2O$ (Galigné & Dumas, 1973). Only in the last paper are the positions of the hydrogen atoms reported.

Experimental

Only one hydrated sodium hypophosphite is on record, with a supposed formula $NaH_2PO_2.H_2O$ (Pascal, 1966), for which morphological (Beckenkamp, 1903) and powder data [*Powder Diffraction File* (1975), card No. 25-832] are also available. However, a thermogravimetric analysis was performed on crystals of commercial product labelled as $NaH_2PO_2.H_2O$, in order to check the water content. Working in a nitrogen stream to avoid oxidation, and with a heating rate of 5 K min^{-1}, a weight loss of 14·0% in the temperature range 303–343 K was observed which corresponded to a loss of 0·8 water molecules, so that the correct formula turned out to be $NaH_2PO_2.\frac{4}{5}H_2O$ or $5NaH_2PO_2.4H_2O$, as was confirmed later by the structure determination.

The monoclinic unit cell and the space group $P2_1/n$ reported in the *Powder Diffraction File* (1975) card No. 25-832 were confirmed by Weissenberg photographs (Cu $K\alpha$ radiation), taking into account systematic extinctions. However, the *hkl* reflexions with $h + k$ odd appeared systematically weaker, indicating the presence of a C pseudo-symmetry which would have then been confirmed by the structural analysis. By refining 25 θ values measured on a single-crystal diffractometer (Mo $K\alpha$ radiation), the following values were obtained: $a = 11{\cdot}127\ (4)$, $b = 13{\cdot}572\ (4)$, $c = 12{\cdot}930\ (4)$ Å, $\beta = 102{\cdot}98\ (8)°$. The morphological cell determined by Beckenkamp (1903) ($a{:}b{:}c = 0{\cdot}8199{:}1{:}2{\cdot}2320$, $\beta = 123°\ 16'$) is obtained by the transformation $\bar{1}00/0\bar{1}0/202$. The forms observed by the same author are transformed as follows: $\{110\} \rightarrow \{11\bar{1}\}$ (dominant), $\{011\} \rightarrow \{02\bar{1}\}$. Other physical data: $Z = 20$, $V = 1902{\cdot}7$ Å^3, $M_r = 102{\cdot}391$, $d_m = 1{\cdot}79$ Mg m^{-3}, $d_c = 1{\cdot}787$ Mg m^{-3}, $F(000) = 1080$, μ(Mo $K\alpha$ radiation) $= 0{\cdot}64$ mm^{-1}.

The diffraction intensities were measured on a colourless irregularly shaped ($0{\cdot}32 \times 0{\cdot}35 \times 0{\cdot}64$ mm) single crystal, sealed in a glass capillary to protect it from deterioration. The measurement conditions, with a Philips PW 1100 four-circle automatic diffractometer, were: Mo $K\alpha$ radiation, graphite monochromator, $\theta \leq 25°$, $\omega/2\theta$ scanning, $\Delta\omega = 2°$, scanning speed 0·04° s^{-1}, background time 10 s on both sides of each peak, attenuating filter inserted for intensities higher than 60 000 counts s^{-1}, three reference reflexions. A final set of 2684 independent observed reflexions, with $I \geq 3\sigma(I)$, was obtained.

Solution and refinement of the structure

The structure was solved by the direct methods program *MULTAN* (Germain, Main & Woolfson, 1971). All the P and Na, and some of the O atoms, appeared in the first solution; the missing O atoms were revealed on a subsequent difference Fourier map. The least-squares refinement with anisotropic thermal factors converged to $R = 0{\cdot}052$. At this stage a difference map showed all the 18 independent hydrogen atoms. Their coordinates and isotropic thermal factors were refined successfully, except for H(5')[*] which gave too long a distance P(5')–H(5') (1·57 Å); therefore H(5') was kept fixed in the position revealed by the difference map. The final full-matrix cycle, with unit weights, led to $R = 0{\cdot}043$; the average values of Δ^2 for groups of reflexions *vs* $|F_o|$ and $\sin\theta$ were satisfactorily constant. The atomic fractional coordinates are reported in Table 1.[†] Because of the striking $C2/c$ pseudo-symmetry showed by the structure, a solution was also searched for by *MULTAN* in the $C2/c$ space group, excluding from the set of *hkl* reflexions all those with $h + k$ odd. The same solution as above, but constrained in the higher symmetry, was found; an attempt to refine it isotropically led to $R = 0{\cdot}205$. Scattering factors for neutral atoms (*International Tables for X-ray Crystallography*, 1962) and the least-squares program of Busing, Martin & Levy (1962) (in a slightly modified version) were used. No absorption or secondary-extinction corrections were applied.

Discussion

Configuration and structural chemistry of the $[H_2PO_2]^-$ *ions*

A large amount of data on the geometry of the hypophosphite ion is provided by the presence of five independent $[H_2PO_2]^-$ ions in this structure, taking into

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[*] A single figure in parentheses denotes an atom of the asymmetric unit; primed figures mean the pseudo-symmetry C operation $\frac{1}{2} + x, -\frac{1}{2} + y, z$. A second figure, ranging from 2 to 4, is included for atoms in the positions $\bar{x},\bar{y},\bar{z}$ and $\pm(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$. Roman numerals represent the following translations: (I) $-\mathbf{c}$; (II) $+\mathbf{c}$; (III) $+\mathbf{a} + \mathbf{b} + \mathbf{c}$; (IV) $-\mathbf{a}$; (V) $+\mathbf{a} + 2\mathbf{b} + \mathbf{c}$; (VI) $+2\mathbf{a} + \mathbf{b} + \mathbf{c}$; (VII) $-\mathbf{b}$; (VIII) $+\mathbf{b}$; (IX) $+\mathbf{a} + \mathbf{b}$; (X) $-\mathbf{a} - \mathbf{c}$; (XI) $-\mathbf{a} + \mathbf{b} - \mathbf{c}$; (XII) $+\mathbf{b} - \mathbf{c}$; (XIII) $-\mathbf{b} - \mathbf{c}$; (XIV) $+2\mathbf{b}$.

[†] Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34232 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates* (×10⁴, *or* ×10³ *for* H *atoms*) *with significant figures of the e.s.d.'s in parentheses*

	x	*y*	*z*
P(1)	96·5 (9)	7980·4 (7)	7531·4 (8)
P(2)	664·7 (9)	8907·2 (8)	793·6 (8)
P(2′)	5393 (1)	3967 (1)	1187 (1)
P(3)	3357 (1)	9425·3 (9)	8630·4 (8)
P(3′)	8419 (1)	4430 (1)	8580·9 (9)
Na(1)	2657 (1)	7395 (1)	25 (1)
Na(2)	3804 (1)	9301 (1)	1457 (1)
Na(2′)	8710 (1)	4376 (1)	1439 (1)
Na(3)	−642 (1)	6739 (1)	−450 (1)
Na(3′)	4268 (1)	1768 (1)	−428 (1)
O(1)	730 (3)	7413 (2)	8491 (2)
O(1′)	5516 (2)	2435 (2)	8447 (2)
O(2)	1851 (2)	8406 (2)	1268 (2)
O(2′)	6681 (3)	3647 (2)	1243 (2)
O(3)	−518 (3)	8337 (2)	562 (2)
O(3′)	4346 (3)	3384 (3)	555 (2)
O(4)	3751 (2)	8872 (2)	9648 (2)
O(4′)	8667 (2)	3957 (2)	9641 (2)
O(5)	4100 (2)	10271 (2)	8377 (2)
O(5′)	9134 (2)	5292 (2)	8350 (2)
W(1)	2879 (3)	10934 (2)	696 (3)
W(1′)	7994 (3)	6004 (2)	699 (3)
W(2)	7421 (3)	7256 (2)	8379 (2)
W(2′)	12314 (3)	2171 (2)	8395 (3)
H(1)	−76 (4)	861 (3)	783 (3)
H(1′)	407 (4)	359 (3)	776 (3)
H(2)	55 (4)	969 (3)	143 (3)
H(2′)	530 (5)	412 (4)	224 (4)
H(3)	76 (4)	936 (3)	−14 (3)
H(3′)	523 (6)	498 (5)	74 (5)
H(4)	309 (5)	886 (4)	780 (4)
H(4′)	796 (5)	394 (5)	778 (5)
H(5)	212 (4)	976 (3)	848 (4)
H(5′)	720	490	840
H(6)	208 (5)	1102 (4)	24 (5)
H(6′)	727 (5)	602 (4)	26 (4)
H(7)	287 (4)	1139 (3)	113 (4)
H(7′)	797 (4)	643 (4)	111 (4)
H(8)	727 (5)	706 (4)	779 (4)
H(8′)	1223 (5)	190 (4)	782 (4)
H(9)	686 (5)	693 (5)	860 (5)
H(9′)	1171 (5)	189 (4)	858 (5)

account that the positions of the hydrogen atoms have been located. Bond lengths and angles are reported in Table 2. A first comment concerns the average values; on the whole, they confirm the values found in the few structures previously studied, though these [with the exception of $Mg(H_2PO_2)_2.6H_2O$ (Galigné & Dumas, 1973)] are not very accurate. If one compares the average distances and angles involving hydrogen atoms with those of the only available neutron-diffraction structure, $Ca(H_2PO_2)_2$ (Loopstra, 1958), a surprisingly good agreement is observed; in fact, the latter values are: P–H, 1·40 and 1·38 Å; H–P–H, 105·3°; O–P–H, 107·2, 109·8, 107·6 and 108·5°. The largest difference is shown by the H–P–H angle, which is significantly lower, on average, in the present study. On the other hand, in the only previous X-ray study where the positions of the H atoms were reported, $Mg(H_2PO_2)_2.6H_2O$, P–H distances of 1·59 (8) Å were obtained, far from the neutron values found in $Ca(H_2PO_2)_2$. The situation of the P–H bond length, where a satisfactory agreement is observed between an average X-ray value and the neutron values, is in contrast to the well known property of the O–H length, which appears systematically shorter by 0·1–0·2 Å in X-ray studies with respect to neutron-diffraction studies. This behaviour should be ascribed to a much smaller polarization of the bonding electrons in the P–H than in the O–H bond, in view of the lower electronegativity of phosphorus with respect to oxygen. The single configurations of the five $[H_2PO_2]^-$ ions show some differences: in particular, distances and angles involving hydrogen atoms are very satisfactory for P(1) and P(2), whereas they get worse for P(2′), P(3) and especially P(3′). On the other hand, P(1) and P(2) show thermal ellipsoids smaller than the other three atoms, and plausibly the higher the thermal motion of P, the lower the accuracy in locating the H atoms which are bonded to it.

Table 2. *Bond lengths* (Å) *and* O–P–O, O–P–H, H–P–H *angles* (°) *in the* $[H_2PO_2]^-$ *ions*

P(1)–O(1)	1·495 (3)		P(2)–O(2)	1·490 (3)	
P(1)–O(1′,4)$^{\mathrm{II}}$	1·492 (3)		P(2) O(3)	1·497 (3)	
P(1)–H(1)	1·40 (4)		P(2)–H(2)	1·37 (4)	
P(1)–H(1′,4)$^{\mathrm{II}}$	1·35 (4)		P(2)–H(3)	1·37 (4)	
P(2′)–O(2′)	1·483 (3)		P(3)–O(4)	1·493 (3)	
P(2′)–O(3′)	1·491 (3)		P(3)–O(5)	1·494 (3)	
P(2′)–H(2′)	1·40 (5)		P(3)–H(4)	1·30 (5)	
P(2′)–H(3′)	1·48 (7)		P(3)–H(5)	1·42 (5)	
P(3′)–O(4′)	1·482 (3)				
P(3′)–O(5′)	1·482 (3)				
P(3′)–H(4′)	1·24 (6)				
P(3′)–H(5′)	1·47				
O(1)···O(1′,4)$^{\mathrm{II}}$	2·577 (4)	119·3 (2)			
O(1)···H(1)	2·34 (4)	108 (2)			
O(1)···H(1′,4)$^{\mathrm{II}}$	2·31 (4)	108 (2)			
O(1′,4)$^{\mathrm{II}}$···H(1)	2·36 (4)	109 (2)			
O(1′,4)$^{\mathrm{II}}$···H(1′,4)$^{\mathrm{II}}$	2·28 (4)	106 (2)			
H(1)···H(1′,4)$^{\mathrm{II}}$	2·18 (6)	105 (3)			
O(2)···O(3)	2·590 (4)	120·3 (2)	O(2′)···O(3′)	2·575 (4)	120·0 (2)
O(2)···H(2)	2·31 (4)	108 (2)	O(2′)···H(2′)	2·30 (5)	106 (2)
O(2)···H(3)	2·34 (4)	109 (2)	O(2′)···H(3′)	2·41 (7)	109 (3)
O(3)···H(2)	2·34 (4)	109 (2)	O(3′)···H(2′)	2·41 (5)	113 (2)
O(3)···H(3)	2·31 (4)	107 (2)	O(3′)···H(3′)	2·36 (7)	105 (3)
H(2)···H(3)	2·14 (6)	102 (3)	H(2′)···H(3′)	2·23 (8)	102 (3)
O(4)···O(5)	2·597 (4)	120·8 (2)	O(4′)···O(5′)	2·594 (4)	122·1 (2)
O(4)···H(4)	2·34 (5)	114 (2)	O(4′)···H(4′)	2·36 (6)	120 (3)
O(4)···H(5)	2·40 (5)	111 (2)	O(4′)···H(5′)	2·39	108
O(5)···H(4)	2·26 (5)	108 (2)	O(5′)···H(4′)	2·28 (6)	113 (3)
O(5)···H(5)	2·34 (5)	107 (2)	O(5′)···H(5′)	2·23	98
H(4)···H(5)	1·97 (7)	93 (3)	H(4′)···H(5′)	1·84	85
$(P{-}O)_{\mathrm{average}}$	1·490				
$(O\cdots O)_{\mathrm{average}}$	2·587				
$(P{-}H)_{\mathrm{average}}$	1·38				
$(O{-}P{-}O)_{\mathrm{average}}$	120·5				
$(O{-}P{-}H)_{\mathrm{average}}$	109				
$(H{-}P{-}H)_{\mathrm{average}}$	97				

The hypophosphite ion $[H_2PO_2]^-$ is characterized by a very distorted tetrahedral configuration, according to an approximate *mm* symmetry: the O—P—O and H—P—H angles are larger and smaller, respectively, than the exact tetrahedral value of 109·47°, while the O—P—H angles are very close to that value. A deformation is then observed from the perfect sp^3 hybridization of the phosphorus atom, which should be the most favourable energetically and is present *e.g.* in the tetrahedral orthophosphate oxyanion $[PO_4]^{3-}$. Indeed replacing two oxygen atoms in $[PO_4]^{3-}$ by as many H atoms allows a shortening of the two P—O distances left, due to the smaller O···H than O···O repulsion; but, just to avoid increasing the repulsion between the remaining O atoms and to minimize that between O and H, the O—P—O and H—P—H angles must become considerably larger and slightly smaller, respectively. Lowering the average P—O bond length from 1·54 Å in $[PO_4]^{3-}$ to 1·49 Å in $[H_2PO_2]^-$ provides an energy gain large enough to balance the distortion of the sp^3 orbitals of the phosphorus atom. The effect of the interatomic repulsion within the hypophosphite ion appears clearly in the case of P(3′), where significantly shorter P—O distances cause the O—P—O angle to widen and, consequently, the H—P—H angle to close.

Pseudo-symmetry and structure topology

A strong $C2/c$ pseudo-symmetry is displayed by the structure (Table 1 and Fig. 1). The P(1) and Na(1) atoms lie approximately on the pseudo-twofold axis and on the pseudo-centre, respectively, corresponding to the special positions 4(*e*) and 4(*d*) of the space group $C2/c$. All the other atoms of the asymmetric unit, including the hydrogen atoms, can be grouped in pairs related by the pseudo-symmetry operation *C*. The Na^+ ions show a rather regular octahedral coordination environment, with Na—O distances ranging between 2·37 and 2·61 Å (Table 3); however, the coordination polyhedra of Na(3) and Na(3′) are characterized by greater values of the average Na—O distance and also by a slightly larger angular distortion, in accordance with their being tied less rigidly to the other polyhedra (*cf.* below). The Na(1) octahedron shares its face O(2)—O(4)$^{\mathrm{I}}$—O(1′,2)$^{\mathrm{III}}$ and its edge O(1)$^{\mathrm{I}}$—O(4′,2)$^{\mathrm{III}}$ with the Na(2) and Na(3) octahedra, respectively; then, by action of the pseudo-symmetry centre on which it lies, it also shares the face O(2′,2)$^{\mathrm{IX}}$—O(4′,2)$^{\mathrm{III}}$—O(1)$^{\mathrm{I}}$ and the edge O(1′,2)$^{\mathrm{III}}$—O(4)$^{\mathrm{I}}$ with the Na(2′,2)$^{\mathrm{IX}}$ and Na(3′,2)$^{\mathrm{IX}}$ octahedra, respectively. Within this group of five independent polyhedra, the sharing of the face O(4)$^{\mathrm{I}}$—O(1′,2)$^{\mathrm{III}}$—O(5,2)$^{\mathrm{V}}$ between the Na(2) and the Na(3′,2)$^{\mathrm{IX}}$ octahedra, and correspondingly of the face O(4′,2)$^{\mathrm{III}}$—O(1)$^{\mathrm{I}}$—O(5′)$^{\mathrm{X}}$ between the Na(2′,2)$^{\mathrm{IX}}$ and the Na(3) polyhedra can also be observed. The action of the *n* plane produces an equivalent group of polyhedra, which is linked to the former by sharing the edge O(5,2)$^{\mathrm{V}}$—O(5′,3)$^{\mathrm{XI}}$ between the Na(2) and the Na(2′,4) octahedra; carrying on, an infinite [101] chain is built up by the Na(1), Na(2), Na(2′,2) and their equivalent (by the *n* operation) polyhedra. This chain is sinusoidally shaped in the (101) plane, and is provided with lateral appendices formed by the Na(3), Na(3,3), Na(3′,2) and Na(3′,4) polyhedra; it is linked to its four adjacent centrosymmetrical chains by sharing the vertices *W*(1′), *W*(1) between the Na(3) and Na(2′), Na(3′) and Na(2) octahedra, respectively. The whole structure is then built up by a system of [101] chains of Na polyhedra, tied to one another by the water molecules *W*(1) and *W*(1′) (Fig. 2).

Hydrogen bonding and dehydration mechanism

The geometrical features of the eight independent hydrogen bonds are reported in Table 4. Distances and angles show regular values, except for the *A*··· *W*···*A*′ angles of *W*(1) and *W*(1′), which are quite small. In their survey of hydrogen bonds studied by neutron diffraction, Ferraris & Franchini-Angela (1972) report for that angle an average value of 110·5°, and a minimum value of 83·4° (excluding bifurcated bonds). An explanation can be found by considering that the two pairs of acceptors of *W*(1) and *W*(1′) form edges of the coordination polyhedra of Na(3,2) and Na(3′,2), respectively; this implies *A*···*A*′ distances much smaller than they are normally, and also smaller *A*··· *W*···*A*′ angles. On the other hand, in order not to reduce the *W*—H···*A* and *W*—H···*A*′ angles excessively, a rotation of the H*W*H′ with respect to the *AWA*′ plane is produced.

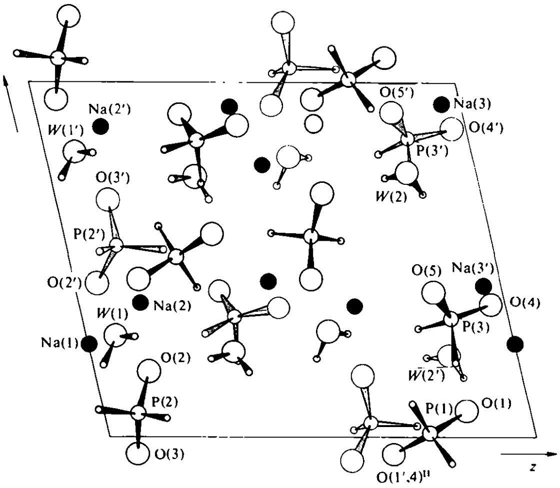

Fig. 1. Half the contents of one unit cell of $NaH_2PO_2.\frac{4}{5}H_2O$ in projection onto the (010) plane. Centrosymmetrically related atoms are not shown; hydrogen atoms are shown as small circles.

Table 3. *Interatomic distances* (Å) *in the* Na *coordination polyhedra*

The e.s.d.'s are 0·003 Å.

$Na(1)–O(1)^{I}$	2·574		
$Na(1)–O(1',2)^{III}$	2·507		
$Na(1)–O(2)$	2·432		
$Na(1)–O(2',2)^{IX}$	2·402		
$Na(1)–O(4)^{I}$	2·450		
$Na(1)–O(4',2)^{III}$	2·452		
Average	2·470		
$Na(2)–O(2)$	2·453	$Na(2')–O(2')$	2·426
$Na(2)–O(4)^{I}$	2·399	$Na(2')–O(4')^{I}$	2·383
$Na(2)–O(1',2)^{III}$	2·469	$Na(2')–O(1,2)^{III}$	2·503
$Na(2)–O(5,2)^{V}$	2·366	$Na(2')–O(5',2)^{VI}$	2·395
$Na(2)–O(5',3)^{XI}$	2·455	$Na(2')–O(5,3)^{XII}$	2·492
$Na(2)–W(1)$	2·547	$Na(2')–W(1')$	2·468
Average	2·448	Average	2·445
$Na(3)–O(1)^{I}$	2·446	$Na(3')–O(1')^{I}$	2·403
$Na(3)–O(3)$	2·521	$Na(3')–O(3')$	2·527
$Na(3)–O(4',2)^{III}$	2·405	$Na(3')–O(4,2)^{III}$	2·373
$Na(3)–O(5')^{X}$	2·480	$Na(3')–O(5)^{XII}$	2·534
$Na(3)–W(1')^{IV}$	2·553	$Na(3')–W(1)^{VII}$	2·606
$Na(3)–W(2)^{X}$	2·442	$Na(3')–W(2')^{X}$	2·420
Average	2·475	Average	2·477

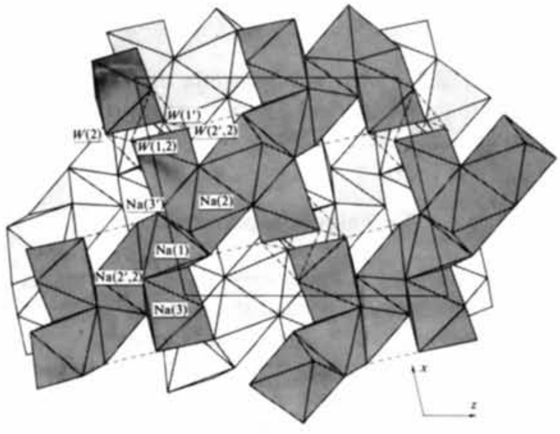

Fig. 2. Coordination polyhedra of the Na atoms and hydrogen bonds (dashed lines) in projection onto the (010) plane.

$W(2)\cdots O(2,3)^{VIII}$ and its pseudo-equivalent bond tie oxygen atoms belonging to the same chain of polyhedra; the other six hydrogen bonds link the six vertices of the two opposite faces $W(1')–W(2)–O(3)$ and $W(1,2)–W(2',2)–O(3',2)$ of the coordination polyhedra of Na(3) and Na(3',2), respectively, which belong to different chains equivalent by **c** translation and lying on the (010) plane. Therefore, a tie is provided by hydrogen bonding between adjacent polyhedra chains not connected by Na–*W* coordination bonds.

The stoichiometric ratio O/Na is quite low in $NaH_2PO_2.\frac{4}{3}H_2O$, because of the small oxidation number of phosphorus in the hypophosphite ion and the little water of hydration present. Then the sodium coordination polyhedra are expected to be strongly condensed by sharing geometrical elements, taking into account that the coordination number is 6 for Na^+ (Catti & Ivaldi, 1977). However, the structure analysis has shown that the condensation of polyhedra is not distributed homogeneously in space, but is concentrated directionally; octahedra share many faces and edges along the [101] chains, whereas the chains themselves are connected very weakly by sharing few vertices between polyhedra and by the hydrogen bonding of water molecules. This topological configuration suggests a reasonable hypothesis for the dehydration mechanism of the crystal, and also for the structure of the anhydrous salt (which is not known); by the loss of the water molecules the polyhedra chains are left unchanged, but are linked more tightly through the sharing of a face instead of a vertex between the Na(3) and Na(2') octahedra. A very limited rearrangement of the initial structure is required by this reaction mechanism to account for the observed low dehydration temperature (about 323 K). A similar case was discussed for the transformation $NaH_2PO_4.2H_2O \rightarrow NaH_2PO_4.H_2O$ (Catti & Ferraris, 1976) in detail (both structures were known).

The X-ray intensities were measured at the Centro di Studio del CNR per la Cristallografia Strutturale, Pavia. Research was supported by the Consiglio Nazionale delle Ricerche, Roma.

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

A	$W\cdots A$	$W–H$	$H\cdots A$	$A\cdots A'$	AWA'	HWH'	WHA
$W(1)–H(6)\cdots O(3,2)^{XIV}$	2·934 (4)	0·96 (6)	2·01 (6)	3·532 (4)	76·2 (1)	100 (5)	161 (5)
$W(1)–H(7)\cdots W(2,2)^{V}$	2·786 (4)	0·84 (5)	1·99 (5)				157 (4)
$W(1')–H(6')\cdots O(3',2)^{IX}$	2·864 (5)	0·88 (5)	2·04 (5)	3·576 (5)	78·4 (1)	105 (5)	157 (5)
$W(1')–H(7')\cdots W(2',2)^{VI}$	2·794 (5)	0·80 (5)	2·05 (5)				157 (5)
$W(2)–H(8)\cdots O(2,3)^{VIII}$	2·807 (4)	0·79 (5)	2·02 (5)	4·595 (4)	110·6 (1)	98 (6)	178 (5)
$W(2)–H(9)\cdots O(3',2)^{III}$	2·781 (4)	0·86 (6)	1·96 (6)				159 (6)
$W(2')–H(8')\cdots O(2',3)$	2·931 (5)	0·82 (6)	2·12 (6)	5·291 (4)	109·0 (1)	96 (6)	169 (5)
$W(2')–H(9')\cdots O(3,2)^{III}$	2·739 (4)	0·85 (6)	1·94 (6)				156 (6)

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Structure Cristalline du Sulfotellurure de Gallium Ga_2S_2Te

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Abstract

The structure of Ga_2S_2Te (M_r = 331·16) has been determined from single-crystal X-ray data. The cell is tetragonal, a = 7·09 (4), c = 10·21 (5) Å, Z = 4, space group $I4_1md$, V = 1918 Å^3, $D_x^{293\,K}$ = 4·03 (8), D_c = 4·08 Mg m^{-3}. The structure was refined to a final R of 0·018. The Ga atoms are in fourfold, the Te atoms in twofold and the S atoms in threefold coordination. This structure is essentially built up of GaS_3Te tetrahedra, which share their four apices in a three-dimensional arrangement. These tetrahedra are linked in chains which form layers parallel to the (001) plane. In two contiguous layers, the chains are successively parallel to the a and b axes.

Introduction

Au cours de l'étude des systèmes Ga_2S_3–Ga_2Te_3, une nouvelle phase, $Ga_2S_{2-x}Te_{1+x}$ ($0 \leq x \leq 0,17$), a été mise en évidence par Maneglier-Lacordaire, Ghémard, Rivet & Flahaut, (1978). Cette phase présente une décomposition péritectique au niveau de la composition Ga_2S_2Te, à la température de 1123 K. Elle est obtenue par union des éléments gallium, tellure et soufre en ampoule de silice scellée sous vide par chauffage progressif jusqu'à 1373 K puis refroidissement lent et recuit à 973 K. Des monocristaux ont été isolés de la préparation. Nous leur avons attribué la formule nominale Ga_2S_2Te.

Techniques expérimentales

Les cristaux sont transparents, de couleur jaune, sans forme géométrique particulière. Nous avons choisi un monocristal de forme sensiblement parallélépipédique, de dimensions 300 × 100 × 80 µm environ. Une étude préliminaire à l'aide d'une chambre de Weissenberg a permis de déterminer la maille cristalline: quadratique, de groupe spatial $I4_1md$ (groupe ponctuel $4mm$) ou $I\bar{4}2d$ (groupe ponctuel $\bar{4}2m$). (hkl: $h + k + l = 2n$; $hhl + l = 4n$.)

Les paramètres ont été affinés à partir des diffractogrammes de poudre en utilisant la méthode des moindres carrés. La masse volumique a été mesurée par pycnométrie à 293 K.

Les intensités de 397 réflexions indépendantes non nulles ont été collectées jusqu'à l'angle $2\theta = 65°$ sur un diffractomètre à quatre cercles Philips en utilisant le rayonnement $K\alpha$ du molybdène (monochromateur de graphite) (μ = 17,0 mm^{-1}).

L'ambiguïté entre les deux groupes spatiaux possibles ne peut pas être levée par l'étude de la répartition statistique de la valeur des modules de facteurs de

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