

many types of metasilicate rings, e.g.  $\text{Si}_3\text{O}_9$ ,  $\text{Si}_4\text{O}_{12}$ ,  $\text{Si}_6\text{O}_{18}$ ,  $\text{Si}_{12}\text{O}_{36}$ .

One peculiarity of the *Sechser-Doppelkette* unit is that, unlike other metasilicate units, it does persist essentially unchanged in a wide variety of structures containing ions of different charges in octahedral sites, e.g.  $M^{2+}$ ,  $M^{3+}$  and  $M^{4+}$ , as well as different numbers of charge-balancing cations. Thus, in the series  $\text{Na}_2\text{LiM}^{3+}\text{Si}_6\text{O}_{15}$ , stable phase formation occurs for octahedral ions as small as  $\text{Fe}^{3+}$  (0.66 Å) and as large as  $\text{Sm}^{3+}$  (0.96 Å). The present structure determination was undertaken because Y (0.90 Å) is amongst the largest trivalent ions which can be substituted in melt-grown crystals.

In the compounds  $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$ ,  $\text{Na}_2\text{LiFeSi}_6\text{O}_{15}$ ,  $\text{NaLiZrSi}_6\text{O}_{15}$  and  $\text{Na}_2\text{LiYSi}_6\text{O}_{15}$  the following features are observed. In the unit cells of these compounds the *c* axis, which is parallel to the direction of propagation of the silicate double chains and is thus a rough measure of the degree to which the chains are folded, lies in the relatively narrow range 10.072–10.375 Å. Also, the Si–O–Si angles are similar in all four. Thus the silicate chain constitutes a stable and relatively inflexible building unit. Again, in all cases there is marked distortion of the bond angles at the tetrahedral site. We

conclude, therefore, that this distortion enables the structure to accommodate a wide range of cations on the octahedral sites without necessitating changes to the *Sechser-Doppelkette* unit.

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## The Structure of Sodium Strontium Phosphate Nonahydrate

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#### Abstract

The crystal structure of  $\text{SrNaPO}_4 \cdot 9\text{H}_2\text{O}$  has been determined by single-crystal X-ray diffraction. The crystals are cubic,  $a = 10.544$  (2) Å, space group  $P2_13$ , with  $Z = 4$ ,  $\rho_m = 2.11$ ,  $\rho_c = 2.083$  g cm<sup>-3</sup>. The structure was refined by full-matrix least-squares techniques to  $R = 0.025$  and  $R_w = 0.026$  for the 323 reflections used in the refinement. All cations and anions are completely surrounded by water molecules. All nine water molecules are coordinated to the same  $\text{Sr}^{2+}$  ion, forming a tricapped trigonal prism. The  $\text{Na}^+$  ion is coordinated to six water molecules, forming a distorted octahedron. Extensive edge-sharing of  $\text{Sr}(\text{H}_2\text{O})_9$  and  $\text{Na}(\text{H}_2\text{O})_6$  polyhedra exists. The environment of the  $\text{PO}_4^{3-}$  ion consists of 15 water molecules all of which

are probably hydrogen bonded to  $\text{PO}_4$  oxygens. However, there is considerable disordering of the phosphate O atoms, somewhat similar to those of  $\text{SO}_4$  groups in alums.

#### Introduction

A large number of struvite-type compounds and their structural relationships have been reported (Dickens & Brown, 1972; Mathew, Kingsbury, Takagi & Brown, 1982; Takagi, Mathew & Brown, 1982). A common feature of these struvite-type compounds (represented by the general formula  $M^{2+}N^+XO_4 \cdot n\text{H}_2\text{O}$  where  $n = 6$  to 8 and  $X = \text{As}$  or  $\text{P}$ ) is that the ionic radius of the monovalent cation is larger than that of the divalent

cation. Banks & Chianelli (1974) have isolated crystals of an Sr compound,  $\text{SrNaPO}_4 \cdot 9\text{H}_2\text{O}$ , and reported that the infrared spectrum of this compound is similar to that of  $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ , a typical member of the struvite series. This would indicate that the structure of  $\text{SrNaPO}_4 \cdot 9\text{H}_2\text{O}$  may be of the struvite type, in spite of the reversal of the radius ratio ( $\text{Sr} > \text{Na}$ ) of the cations and the excess of water molecules. The crystal structure of  $\text{SrNaPO}_4 \cdot 9\text{H}_2\text{O}$  was investigated with the objective of relating it to struvite-type compounds.

### Experimental

Crystals of  $\text{SrNaPO}_4 \cdot 9\text{H}_2\text{O}$  were prepared by a modification of the diffusion method used by Banks, Chianelli & Pintchovsky (1973). Solutions of  $\text{Sr}(\text{NO}_3)_2$  and  $\text{Na}_2\text{HPO}_4$  were allowed to diffuse into a medium containing a sodium barbiturate/barbital buffer at pH 7.7 at room temperature. Large octahedral crystals of  $\text{SrNaPO}_4 \cdot 9\text{H}_2\text{O}$  were obtained within a few days. The X-ray powder pattern, the cell parameter and the refractive index agreed with those reported by Banks & Chianelli (1974).

Precession photographs showed cubic symmetry  $m\bar{3}$ . Systematic absences of  $h00$  for  $h = 2n + 1$  indicated the space group to be  $P2_13$ , which was confirmed by the structure analysis.

An approximately octahedral crystal with a mean diagonal dimension of 0.13 mm was used for the measurement of cell parameters and intensity data. All measurements were made on a Syntex\* automatic diffractometer with graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ). The cell parameter was obtained by a least-squares fit of 15  $2\theta$  values with  $19 < 2\theta < 32^\circ$  by automatically centering at positive  $2\theta$  values. Crystal data are given in the *Abstract*.

All reflections in the  $hkl$  octant, up to  $2\theta = 50^\circ$ , were measured using the  $\theta$ - $2\theta$  scan technique and a variable scan rate of  $0.5^\circ \text{ min}^{-1}$  to  $29.3^\circ \text{ min}^{-1}$ , depending on the intensity of each reflection. The backgrounds were counted for half the scan time at each end of the scan range. Four reflections, measured periodically, showed about 8% decrease in their intensities during the data collection. The intensities were corrected for this change in scale factors, Lorentz and polarization effects and for absorption [ $\mu(\text{Mo } K\alpha) = 46.8 \text{ cm}^{-1}$ ] using XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). The maximum and minimum absorption corrections to intensities were 1.648 and 1.528, respectively. The 1477 reflections measured

were merged into a unique set of 409 reflections, of which 323 with  $F_o > 3\sigma(F_o)$  were used in the structure analysis and refinements. The equivalent reflections agreed within 3.6% on average (based on  $F$ ).

### Structure solution and refinement

Since  $Z = 4$ , all heavy atoms, Sr, Na and P, must be in the special positions,  $4(a)$ , along the threefold axis. Their positions were deduced from a three-dimensional Patterson synthesis. The positions of the remaining atoms were located in a subsequent Fourier synthesis.

All refinements were made by the full-matrix least-squares program *RFINE4* (Finger & Prince, 1975). The quantity minimized was  $\sum w(|F_o| - |F_c|)^2$  where  $w$  is the weight derived from counting statistics. The scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974).

Refinement of the structure proceeded smoothly and converged to  $R (= \sum ||F_o| - |F_c|| / \sum |F_o|)$  and  $R_w \{= [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}\}$  values of 0.070 and 0.086, respectively. However, the O atoms of the phosphate group had large thermal parameters indicating disorder, whereas the remaining atoms including the water molecules had normal thermal parameters. A difference Fourier synthesis showed two distinct peaks ( $1.6$  and  $2.0 \text{ e \AA}^{-3}$ ) around the P atom approximately  $1.5 \text{ \AA}$  away from P. These two peaks were assigned to O atoms in general positions. Thus the O atom in the general position is statistically disordered to occupy three different positions, O(11), O(12) and O(13), (not related by the threefold operation) and their occupancy factors were initially fixed at 50, 25 and 25%, respectively, on the basis of the electron density. Although the thermal parameters and residual electron density around O(1) (the O atom in the special position along the threefold axis) indicated considerable disordering of O(1) also, it was not possible to resolve this O into three sets of positional parameters. Therefore, it was fixed at the average position on the threefold axis with a full occupancy factor.

In subsequent refinements Sr, Na, P, O(1) and the water molecules were refined with anisotropic thermal parameters and the disordered phosphate O atoms with isotropic thermal parameters. The H atoms were located in a difference Fourier synthesis. Their positional parameters were also refined in subsequent calculations, with a fixed isotropic thermal parameter ( $B = 2.5 \text{ \AA}^2$ ). The occupancy factors for O(11), O(12) and O(13) were also refined with the constraint that the total occupancy was 1.0 and their thermal parameters were equal. The occupancy factors refined to 0.50, 0.26 and 0.24 for O(11), O(12) and O(13), respectively. When these disordered O atoms were refined with independent anisotropic thermal parameters, the

\* Certain commercial materials and equipment are identified in this article to specify the experimental procedure. In no instance does such identification imply recommendation or endorsement by the National Bureau of Standards or that the materials and equipment identified are necessarily the best available for the purpose.

Table 1. Final atomic parameters of non-hydrogen atoms ( $\times 10^4$ ) and hydrogen atoms ( $\times 10^3$ ) in  $\text{SrNaPO}_4 \cdot 9\text{H}_2\text{O}$

Throughout this report, the numbers in parentheses are standard deviations in the least significant digits given.

	x	y	z	$B_{\text{eq}}^*$ ( $\text{\AA}^2$ )
Sr	5532 (1)	x	x	1.26 (3)
Na	1767 (3)	x	x	2.36 (10)
P	9243 (2)	x	x	1.18 (5)
O(1)	9426 (8)	x	x	9.7 (5)
O(11)†	590 (11)	3628 (9)	4465 (9)	2.8 (5)
O(12)†	1187 (17)	4703 (19)	4499 (20)	3.3 (6)
O(13)†	1809 (20)	3971 (21)	4814 (19)	1.4 (6)
O(w1)	3674 (5)	456 (6)	7088 (5)	2.2 (3)
O(w2)	1012 (5)	808 (5)	6517 (5)	2.5 (3)
O(w3)	2081 (5)	1485 (6)	4004 (6)	2.3 (3)
H(11)	414 (8)	57 (9)	660 (7)	
H(12)	318 (8)	69 (9)	687 (9)	
H(21)	56 (7)	53 (8)	705 (7)	
H(22)	90 (7)	163 (8)	675 (7)	
H(31)	294 (8)	129 (7)	403 (7)	
H(32)	197 (8)	216 (7)	429 (7)	

\* The equivalent values of the anisotropic temperature factors correspond to the definitions given by Hamilton (1959). Fixed isotropic thermal parameters ( $B_0 = 2.5 \text{\AA}^2$ ) were used for all H atoms.

† The O atom in the general position is statistically disordered to occupy three different positions, O(11), O(12) and O(13) (not related by the threefold operation) with occupancy factors of 50, 29 and 21%, respectively. O(12) and O(13) were refined with isotropic thermal parameters.

thermal parameters for O(13) were non-positive definite. Therefore, the disordered O atoms O(12) and O(13) were refined with isotropic thermal parameters whereas all the remaining non-hydrogen atoms were refined with anisotropic thermal parameters. An isotropic secondary-extinction correction (Zachariasen, 1967) was applied and the extinction parameter was refined to  $0.4 (1) \times 10^{-4} \text{ cm}^{-1}$ . The occupancy factors for O(11), O(12) and O(13) refined to 0.50 (1), 0.29 (2) and 0.21 (2), respectively. The goodness of fit was 0.85 and final average and maximum shift-to-error ratios for the atomic parameters were 0.02 and 0.11, respectively. Final  $R$  and  $R_w$  values were 0.025 and 0.026 for the 323 reflections used in the refinement and 0.039 and 0.029 for all reflections. Final atomic parameters are listed in Table 1.\*

In the final difference Fourier synthesis, there were residual electron densities around the disordered phosphate group. This, together with the anomalous thermal parameters of the phosphate O atoms, would indicate that the disordering of the  $\text{PO}_4$  group may be more complex than assumed in this refinement.

\* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36635 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## Results and discussion

The Sr, Na and P atoms in  $\text{SrNaPO}_4 \cdot 9\text{H}_2\text{O}$  are at special positions 4(a) along the threefold axis, whereas the water molecules are in general positions. Although all nine water molecules are coordinated to the same  $\text{Sr}^{2+}$  ion, the overall arrangement is such that all the ions  $\text{Sr}^{2+}$ ,  $\text{Na}^+$  and  $\text{PO}_4^{3-}$  are completely surrounded by water molecules (Fig. 1). The  $\text{Sr}(\text{H}_2\text{O})_9$  polyhedra and  $\text{Na}(\text{H}_2\text{O})_6$  octahedra are linked together extensively and the interstitial space is occupied by the disordered phosphate groups.

The  $\text{Sr}^{2+}$  ion is coordinated to nine water molecules with a mean Sr—O(w) distance of 2.668 Å (Table 2). To our knowledge, this is the first example of ninefold hydration of the  $\text{Sr}^{2+}$  ion in the crystalline state. The geometry of  $\text{Sr}(\text{H}_2\text{O})_9$  corresponds to a tricapped trigonal prism. The sets of water molecules, O(w1) and O(w2), related by the threefold axis constitute a trigonal prism and the O(w3) molecules cap the prism faces. The shortest Sr—O(w) distances involve the three water molecules, O(w2), which are not part of the  $\text{Na}^+$ -ion environment [Sr—O(w2) = 2.631 Å]. The longest Sr—O(w) bonds are to water molecules O(w3), on the capped faces [Sr—O(w3) = 2.726 Å], as expected. Although no direct comparison is possible due to lack of data on similarly hydrated  $\text{Sr}^{2+}$  ions, some comparisons may be made with some related Sr compounds. In  $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , the  $\text{Sr}^{2+}$  ion is coordinated to eight water molecules arranged in a square antiprism with an Sr—O(w) distance of 2.60 (3) Å (Smith, 1953). In  $\text{Sr}_3(\text{P}_3\text{O}_9)_2 \cdot 7\text{H}_2\text{O}$  (Tordjman, Durif & Guitel, 1976) and  $\text{SrNa}(\text{P}_3\text{O}_9) \cdot 3\text{H}_2\text{O}$  (Zilber, Tordjman, Durif & Guitel, 1974),  $\text{Sr}^{2+}$  has nine coordination, six  $\text{P}_3\text{O}_9$  oxygens forming a trigonal prism and three from water molecules capping the prism faces. Thus the environments of the  $\text{Sr}^{2+}$  ions in these two compounds are quite similar to that in  $\text{SrNa}(\text{PO}_4) \cdot 9\text{H}_2\text{O}$ . Mean Sr—O bond lengths in  $\text{Sr}_3(\text{P}_3\text{O}_9)_2 \cdot 7\text{H}_2\text{O}$  and  $\text{SrNa}(\text{P}_3\text{O}_9) \cdot 3\text{H}_2\text{O}$  are 2.66 and 2.62 Å, respectively, and compare well with the present value of 2.668 Å.

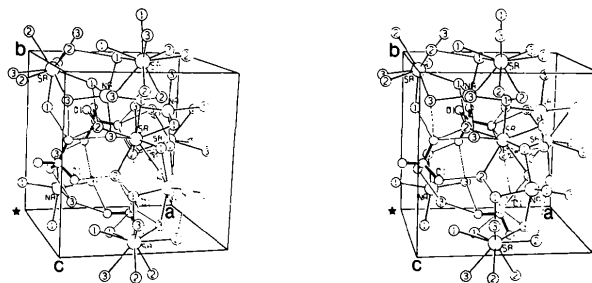


Fig. 1. A stereoscopic illustration of the unit-cell contents in  $\text{SrNaPO}_4 \cdot 9\text{H}_2\text{O}$ . The origin is labeled with a star. The components of the disordered phosphate, O(12) and O(13) and some labels are omitted for clarity. The independent water molecules, O(w1), O(w2) and O(w3), are identified by numbers 1, 2 and 3, respectively.

Table 2. Selected bond lengths (Å) and bond angles (°) for SrNaPO<sub>4</sub>·9H<sub>2</sub>O

Sr...O(w1)	×3	2.647 (5)	P—O(1)		1.492 (9)
Sr...O(w2)	×3	2.631 (5)	P—O(11)	×3	1.519 (10)
Sr...O(w3)	×3	2.726 (6)	P—O(12)	×3	1.483 (21)
Na...O(w1)	×3	2.413 (7)	P—O(13)	×3	1.517 (21)
Na...O(w3)	×3	2.400 (7)			
O(w1)—Sr—O(w1')	×3	74.8 (2)	O(w1)—Sr—O(w3'')	×3	134.5 (2)
O(w1)—Sr—O(w2)	×3	134.6 (2)	O(w2)—Sr—O(w2')	×3	79.6 (2)
O(w1)—Sr—O(w2')	×3	87.9 (2)	O(w2)—Sr—O(w3)	×3	67.2 (2)
O(w1)—Sr—O(w2'')	×3	140.8 (2)	O(w2)—Sr—O(w3')	×3	137.6 (2)
O(w1)—Sr—O(w3)	×3	67.5 (2)	O(w2)—Sr—O(w3'')	×3	69.3 (2)
O(w1)—Sr—O(w3')	×3	71.6 (2)	O(w3)—Sr—O(w3')	×3	120.0 (2)
O(w1)—Na—O(w1')	×3	88.6 (2)	O(w1)—Na—O(w3'')	×3	155.7 (2)
O(w1)—Na—O(w3)	×3	76.6 (2)	O(w3)—Na—O(w3')	×3	90.2 (2)
O(w1)—Na—O(w3')	×3	109.9 (2)			
O(1)—P—O(11)	×3	109.8 (5)	O(11)—P—O(13')		163.2 (9)
O(1)—P—O(12)	×3	121.9 (8)	O(11)—P—O(13'')		77.4 (9)
O(1)—P—O(13)	×3	81.2 (9)	O(12)—P—O(12')	×3	94.6 (1.1)
O(11)—P—O(11')	×3	109.2 (6)	O(12)—P—O(13)		41.6 (1.1)
O(11)—P—O(12)		51.2 (9)	O(12)—P—O(13')		112.4 (1.1)
O(11)—P—O(12')		128.2 (9)	O(12)—P—O(13'')		127.5 (1.1)
O(11)—P—O(12'')		58.2 (9)	O(13)—P—O(13')	×3	117.7 (1.1)
O(11)—P—O(13)		54.3 (9)			

The Na<sup>+</sup> ion is coordinated to six water molecules forming a distorted octahedron. Na—O(w) distances are 2.400 and 2.413 Å which are in the normal range of values found in other Na hydrates.

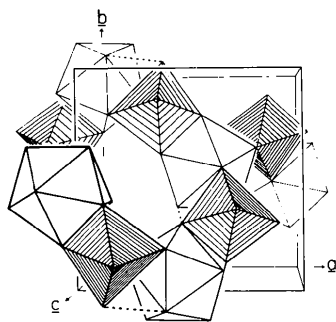


Fig. 2. The packing of Sr(H<sub>2</sub>O)<sub>9</sub> polyhedra and Na(H<sub>2</sub>O)<sub>6</sub> octahedra. The broken lines indicate hydrogen bonding between the water molecules of the cation polyhedra.

Each Sr(H<sub>2</sub>O)<sub>9</sub> polyhedron shares three edges, O(w1)—O(w3), with three different Na(H<sub>2</sub>O)<sub>6</sub> octahedra related by the threefold axis (Figs. 1 and 2). Each Na(H<sub>2</sub>O)<sub>6</sub> octahedron shares three edges with Sr(H<sub>2</sub>O)<sub>9</sub> polyhedra. In addition to the edge-sharing linkage, these polyhedra are also linked by the O(w1)—H(12)···O(w2) hydrogen bond (Table 3).

The anomalous thermal parameters of the PO<sub>4</sub> group in this study, particularly those of O(1), bear considerable resemblance to those of the SO<sub>4</sub> groups in alums. In both cases, the PO<sub>4</sub><sup>3-</sup> or SO<sub>4</sub><sup>2-</sup> ion lies on a threefold axis with the P or S atom and one O atom, O(1), on the threefold axis. The anomalous behavior of the SO<sub>4</sub> groups in alums has been explained in terms of a disorder by the inversion of a fraction of the SO<sub>4</sub> groups through the S-atom position and that this fraction tends to increase as the size of the monovalent cation decreases (Larson & Cromer, 1967). However, Ledsham, Steeple & Hughes (1970) have proposed that the O atoms are more probably subject to extreme thermal motion, the nature of which is difficult to postulate without violation of the space-group symmetry requirements.

The final difference Fourier synthesis for SrNaPO<sub>4</sub>·9H<sub>2</sub>O showed a residual electron density of 0.6 e Å<sup>-3</sup> along the threefold axis at x = 0.008 corresponding to the possible position of O(1') [inverted position of O(1)]. However, we could not identify any additional residual electron density for the corresponding positions of the remaining O atoms (consistent with the tetrahedral geometry of the PO<sub>4</sub> group). The P—O(1') bond is in the direction of the Na<sup>+</sup> ion on the threefold axis. Although the O(1')···Na contact of 3.12 Å does not indicate any significant interaction, O(1') would be pointed towards a face [O(w1)—O(w1')—O(w1'')] of the Na(H<sub>2</sub>O)<sub>6</sub> octahedron. The O(1')···O(w1) distance of 2.60 Å would indicate a strong hydrogen bond, but the geometry around O(1') [P—O(1')—O(w1) = 130.8°,

Table 3. Details of the hydrogen bonds in NaSrPO<sub>4</sub>·9H<sub>2</sub>O

D—H···A*	Position of A	D—H (Å)	H···A (Å)	D···A (Å)	∠D—H···A (°)
O(w1)—H(11)···O(11)	[½ + x, ½ - y, 1 - z]	0.72 (8)	2.08 (8)	2.774 (12)	163 (9)
O(w1)—H(11)···O(12)	[z, y, z]		2.14 (8)	2.770 (21)	147 (9)
O(w1)—H(12)···O(w2)	[x, y, z]	0.62 (9)	2.32 (8)	2.895 (8)	155 (11)
O(w2)—H(21)···O(11)	[½ - z, x, ½ + y]	0.79 (8)	2.04 (8)	2.717 (11)	143 (7)
O(w2)—H(21)···O(12)	[y - ½, ½ - z, 1 - x]		2.07 (8)	2.805 (19)	155 (8)
O(w2)—H(21)···O(13)	[y - ½, ½ - z, 1 - x]		2.09 (8)	2.860 (22)	162 (8)
O(w2)—H(22)···O(1)	[1 - x, y - ½, ½ - z]	0.91 (8)	2.03 (8)	2.824 (10)	145 (7)
O(w2)—H(22)···O(13)	[z - ½, ½ - x, 1 - y]		2.14 (8)	2.859 (22)	135 (7)
O(w3)—H(31)···O(11)	[z, x, y]	0.93 (8)	1.82 (8)	2.714 (12)	161 (7)
O(w3)—H(31)···O(12)	[z, x, y]		1.79 (8)	2.672 (22)	157 (7)
O(w3)—H(31)···O(13)	[z, x, y]		2.05 (9)	2.902 (21)	152 (7)
O(w3)—H(32)···O(11)	[x, y, z]	0.78 (7)	2.13 (8)	2.795 (12)	143 (7)
O(w3)—H(32)···O(13)	[x, y, z]		2.00 (8)	2.772 (23)	172 (8)

\* Donor—Hydrogen···Acceptor. D—H at x, y, z.

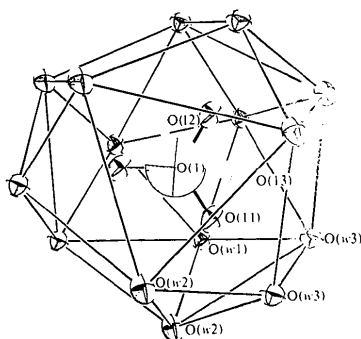


Fig. 3. A view down the bond O(1)–P (along the threefold axis) showing the distribution of the water molecules around the disordered  $\text{PO}_4$  group.

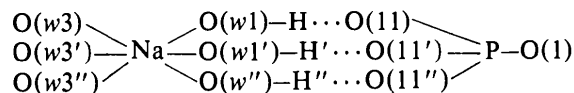
$\text{O}(w1)–\text{O}(1')–\text{O}(w1') = 81.8^\circ$ ] does not support this view. Furthermore, if the  $\text{O}(1') \cdots \text{O}(w1)$  contacts were strong hydrogen bonds, a significantly larger proportion of the  $\text{PO}_4$  group would have been in the inverted configuration.

The disordered O positions, O(12) and O(13), cannot be accounted for by a simple rotational disorder. The disorder of the  $\text{PO}_4$  group may be visualized as a combination of a rotational disorder [about bond O(1)–P by about  $50^\circ$ ] and a rocking motion pivoted at the P atom which could account for the extreme thermal parameters of O(1) as well as the distortions of the O–P–O angles (Table 2).

The environment of the  $\text{PO}_4^{3-}$  ion consists of 15 water molecules (Fig. 3), associated with six  $\text{Sr}(\text{H}_2\text{O})_9$  polyhedra and four  $\text{Na}(\text{H}_2\text{O})_6$  octahedra. Thus the positions of the water molecules are primarily controlled by the cations. O(1), on the threefold axis, accepts three hydrogen bonds from three different water molecules, O(w2). The geometry around O(11) (the major component of the disordered O atom in the general position) suggests hydrogen bonding to four water molecules (Table 3). Thus, all 15 water molecules appear to be hydrogen bonded to phosphate O atoms. Assuming the coordination geometry of a  $\text{PO}_4$

oxygen to be tetrahedral, one would expect the hydration number of the  $\text{PO}_4^{3-}$  ion to be 12. Such configurations of hydrogen-bonded water molecules around the  $\text{PO}_4^{3-}$  ion have been observed in several crystalline hydrates (Schroeder, Mathew & Brown, 1978; Mathew *et al.*, 1982). The disorder of the  $\text{PO}_4^{3-}$  ion in the present study may be related to the overcrowding of the water molecules around it. In addition, the phosphate O atoms can form hydrogen bonds with the same H atom, whether the O is in positions O(11), O(12) or O(13) (Table 3). This could account for the preferred orientation sites of the phosphate O atoms.

One face of the  $\text{PO}_4$  tetrahedron [O(11)–O(11')–O(11'')] is linked to a face of the  $\text{Na}(\text{H}_2\text{O})_6$  octahedron [O(w1)–O(w1')–O(w1'')], *via* hydrogen bonds, as shown below.



Face linkage of the  $\text{PO}_4^{3-}$  ion with hydrated cations is known in several magnesium phosphates, *e.g.*  $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$  (Schroeder *et al.*, 1978),  $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$  (Mathew & Schroeder, 1979), and  $\text{MgNaPO}_4 \cdot 7\text{H}_2\text{O}$  (Mathew *et al.*, 1982).

Struvite analogues of the type  $\text{MgMPO}_4 \cdot 6\text{H}_2\text{O}$  ( $M = \text{K}, \text{Rb}, \text{Cs}, \text{Tl}, \text{NH}_4$ ) have been reported by Banks, Chianelli & Korenstein (1975). Although these compounds appear to be isomorphous, there are substantial differences in their structures.  $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$  are orthorhombic (isomorphous) and contain a direct contact between phosphate O and the  $\text{K}^+/\text{NH}_4^+$  ion. With the increasing size of the monovalent ion, higher-symmetry forms are preferred; for example,  $\text{MgCsPO}_4 \cdot 6\text{H}_2\text{O}$  exists in a hexagonal and a cubic form (Banks *et al.*, 1975). Although the structural details of  $\text{MgCsPO}_4 \cdot 6\text{H}_2\text{O}$  are unknown, some comparison can be made with the probably isostructural arsenate

Table 4. *Crystal data of some struvite-type compounds*

Compound	System	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å <sup>3</sup> )	<i>Z</i>	Space group	Reference
$\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$	Orthorhombic	6.941	6.137	11.199	477.0	2	$Pmn2_1$	(a)
$\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$	Orthorhombic	6.873	6.160	11.087	469.4	2	$Pmn2_1$	(b)
$\text{MgCsPO}_4 \cdot 6\text{H}_2\text{O}$	Hexagonal	6.899		11.99	484.2	2	$P6_3mc$	(c)
$\text{MgCsPO}_4 \cdot 6\text{H}_2\text{O}$	Cubic	10.02			1006.0	4	$F43m$	(c)
	(pseudo cell)	7.085	7.085	10.02	503.0	2		
$\text{MgNaPO}_4 \cdot 7\text{H}_2\text{O}$	Tetragonal	6.731		10.982	497.6	2	$P4_2/mmc$	(d)
$\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$	Orthorhombic	7.140	7.146	11.696	593.4	2	$Amm2$	(e)
$\text{SrNaPO}_4 \cdot 9\text{H}_2\text{O}$	Cubic	10.544			1172.2	4	$P2_13$	(f)
	(pseudo cell)	7.456	7.456	10.544	586.1	2		

References: (a) Whitaker & Jeffery (1970). (b) Mathew & Schroeder (1979). (c) Banks *et al.* (1975). (d) Mathew *et al.* (1982). (e) Dickens & Brown (1972). (f) This work.

analogue, the cubic form of  $\text{MgCsAsO}_4 \cdot 6\text{H}_2\text{O}$ . In this compound the  $\text{AsO}_4^{3-}$  ion is on the body diagonal (on a threefold axis) and all ions are completely surrounded by water molecules (Ferrari, Cavalca & Nardelli, 1955). Thus the structure of  $\text{SrNaPO}_4 \cdot 9\text{H}_2\text{O}$  is related to  $\text{MgCsAsO}_4 \cdot 6\text{H}_2\text{O}$ , a typical member of the struvite series. The cell dimensions of the cubic form of  $\text{MgCsPO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{SrNaPO}_4 \cdot 9\text{H}_2\text{O}$  are also comparable and the pseudocells (Table 4) resemble the orthorhombic cell of struvite. The chemical relationship is more obvious if the formulae are written  $[\text{Mg}(\text{H}_2\text{O})_6]_1[\text{CsPO}_4]$  and  $[\text{Sr}(\text{H}_2\text{O})_9]_1[\text{NaPO}_4]$ .

Crystal data of selected 'struvite-type' compounds are listed in Table 4. In spite of the wide variations in composition, the general features of the structures are similar. In  $\text{Mg}^{2+}$ -containing struvite-type compounds in Table 4 (except for  $\text{MgCsPO}_4 \cdot 6\text{H}_2\text{O}$ ), an interpenetrating layer-type structure consisting of  $[\text{Mg}(\text{H}_2\text{O})_6(\text{PO}_4)]$  acts as a host lattice and the remaining water molecules and the monovalent cation occupy interstitial spaces. In  $\text{MgCsPO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{SrNaPO}_4 \cdot 9\text{H}_2\text{O}$  and  $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$ , the hydrated cation species define the host lattice and the  $\text{XO}_4^{3-}$  ions occupy the interstitial space. These differences in the structural details can be related to the ionic size and the coordinations of the cations. The wide range of symmetries observed in these struvite-type compounds is indicative of the different types of linkages of hydrated cation polyhedra and/or the  $\text{XO}_4$  tetrahedra.

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