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Crystal Structure of $Na_3PO_4 \cdot \frac{1}{2}H_2O$

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The crystal structure of trisodium monophosphate hemihydrate was determined. The space group is *C2/c* and a unit cell contains eight formula units. The unit cell dimensions of $Na_3PO_4 \cdot \frac{1}{2}H_2O$ are a = 9.631(3), b = 5.416(2), c = 16.938(8) Å, β = 102.60(5)°. The final R value is 0.027 for a set of 1430 independent reflections. This atomic arrangement is mainly a three-dimensional network of distorted NaO_6 octahedra. The hydrogen bonding scheme is given.

Introduction

Trisodium monophosphate hemihydrate has been characterized during various investigations of the H_2O–P_2O_5–Na_2O system (*1–4*), but up to now the crystal structure of this salt has not been investigated.

Chemical Preparation

$Na_3PO_4 \cdot \frac{1}{2}H_2O$ crystals were obtained during experiments run for the preparation of Na_3PO_4(H.T.) crystals. Schematically the reaction used here is

$$AlPO_4 + 4NaOH \rightarrow Na_3PO_4 + NaAlO_2.$$

The aluminum monophosphate is dissolved in a concentrated sodium hydroxide solution which is then slowly evaporated at low temperature (60–80°C). Crystals of $Na_3PO_4 \cdot \frac{1}{2}H_2O$ appear when the temperature is approximately 60°C. They are stout monoclinic prisms, apparently very stable at room temperature since their preparation more than 2 months ago.

Crystal Data and Structure Determination

$Na_3PO_4 \cdot \frac{1}{2}H_2O$ is monoclinic with the unit cell dimensions a = 9.631(3), b = 5.416(2), c = 16.938(8) Å, β = 102.60(5)°. There are eight formula units per cell and the calculated density is 2.657. The observed extinction conditions

$$h\,k\,l \text{ with } h + k = 2n,$$
$$h\,0\,l \text{ with } h = 2n \text{ and } 1 = 2n$$

correspond to *Cc* or *C2/c* as possible space groups. The structure determination will show that the centrosymmetrical *C2/c* is the correct one.

A prismatic crystal (0.32 × 0.26 × 0.26 mm^3) was chosen for the measurements on a Philips PW 1100 four-circle automatic diffractometer operating with silver $K\alpha$ radiation (0.5608 Å) monochromatized by a graphite plate. The intensities of 1755 reflections with $\theta < 30°$ were measured, using the following conditions: ω-scan, scan speed 0.03° sec^{-1}, scan width 1.20°. Back-

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TABLE I

ATOMIC COORDINATES

Atom	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	$B_{eq.}(\sigma)$
P	0.15691(4)	0.38662(7)	0.11307(2)	0.700(5)
Na(1)	0.18100(8)	0.5305(1)	0.95193(4)	1.38(1)
Na(2)	0.00084(9)	0.0973(2)	0.59730(5)	1.83(1)
Na(3)	0.64975(7)	0.1680(1)	0.78490(4)	1.22(1)
O(W)	0.0000(0)	0.9551(3)	0.25000(0)	1.63(3)
O(1)	0.1013(1)	0.2354(2)	0.03580(7)	1.28(2)
O(2)	0.0324(1)	0.5265(2)	0.64902(7)	1.29(2)
O(3)	0.7564(1)	0.2800(2)	0.67431(7)	1.31(2)
O(4)	0.7412(1)	0.1124(2)	0.09349(7)	1.32(2)
H	0.429(3)	0.357(6)	0.229(2)	3.1(7)

Note. The estimated standard deviations are given in parentheses. Thermal factors are $B_{eq.}$ for nonhydrogen atoms and $B_{iso.}$ for hydrogen atoms.

TABLE II

ANISOTROPIC THERMAL PARAMETERS β_{ij} FOR NONHYDROGEN ATOMS

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P	0.00201(2)	0.00548(7)	0.00068(1)	−0.0004(1)	0.00050(2)	0.00006(6)
Na(1)	0.00498(6)	0.0105(2)	0.00098(2)	−0.0046(2)	0.00042(6)	0.0012(1)
Na(2)	0.00688(8)	0.0122(2)	0.00142(2)	0.0057(2)	0.00098(7)	−0.0003(1)
Na(3)	0.00377(6)	0.0110(2)	0.00092(2)	0.0008(2)	0.00072(5)	0.0003(1)
O(W)	0.00397(15)	0.0081(4)	0.00217(6)	0.0000(0)	0.00031(16)	0.0000(0)
O(1)	0.00512(11)	0.0090(3)	0.00085(3)	−0.0049(3)	0.00074(9)	−0.0011(2)
O(2)	0.00283(9)	0.0149(3)	0.00110(3)	−0.0037(3)	0.00129(8)	−0.0008(2)
O(3)	0.00343(9)	0.0111(3)	0.00125(3)	−0.0043(3)	0.00052(9)	−0.0021(2)
O(4)	0.00499(10)	0.0092(3)	0.00098(3)	−0.0070(3)	0.00075(9)	0.0003(2)

Note. Estimated standard deviations are given in parentheses. The formula used here is

$$T = \beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl.$$

ground was measured during 5 sec at each extremity of the scan domain. Two reference reflections $\bar{1}\ 3\ 6$ and $1\ \bar{3}\ \bar{6}$) were measured every 2 hr without any significant variation. A final set of 1715 independent observations was obtained from this measurement. No absorption correction was made.

The crystal structure was solved by using classical methods: study of the Patterson function followed by successive Fourier syntheses. After some refinement cycles with anisotropic thermal parameters the R value is 0.028 for a set of 1430 reflections such that

$$F_0 > 2\sigma_F,$$
$$F_0 - F_c < 20 \quad \text{in a scale 0–1026.}$$

At this stage a difference Fourier map revealed the hydrogen atoms. Final refinement cycles, including the hydrogen atoms (with isotropic thermal factors), gave a final R value of 0.027 with the same set of reflections.

Table I reports the final atomic coordinates with the calculated $B_{eq.}$ for nonhydrogen atoms and $B_{iso.}$ for hydrogen atoms. All atoms are in the general position of the $C2/c$ space group with the exception of the water

TABLE III

MAIN INTERATOMIC DISTANCES AND BOND ANGLES IN THE PO_4 TETRAHEDRON

P	O(1*a*)	O(2*e*)	O(3*g*)	O(4*e*)
O(1*a*)	$\underline{1.540(2)}$	2.521(2)	2.498(2)	2.524(2)
O(2*e*)	110.24(10)	$\underline{1.533(2)}$	2.513(2)	2.515(2)
O(3*g*)	108.23(10)	109.61(9)	$\underline{1.542(2)}$	2.517(2)
O(4*e*)	109.82(9)	109.64(10)	109.28(10)	$\underline{1.544(2)}$

TABLE IV

Main Interatomic Distances and Bond Angles in the NaO_6 Polyhedra

$Na(1)O_6$ polyhedron

Na(1)	O(1*a*)	O(1*d*)	O(2*f*)	O(3*f*)	O(4*b*)	O(4*c*)
O(1*a*)	2.377(2)	3.350(4)	3.498(2)	4.099(2)	4.588(2)	2.524(2)
O(1*d*)	86.42(7)	2.514(2)	4.412(2)	2.498(2)	3.686(3)	3.482(2)
O(2*f*)	94.86(7)	129.05(7)	2.372(2)	3.088(2)	3.381(2)	4.403(2)
O(3*f*)	107.07(7)	56.92(5)	74.41(6)	2.714(2)	3.556(2)	4.896(2)
O(4*b*)	161.91(8)	100.67(7)	93.47(7)	90.62(7)	2.269(2)	3.545(3)
O(4*c*)	63.95(6)	90.46(7)	135.31(7)	147.25(7)	99.10(6)	2.388(2)

$Na(2)O_6$ polyhedron

Na(2)	O(W)	O(1*e*)	O(1*f*)	O(2*a*)	O(4*e*)	O(4*g*)
O(W)	2.611(1)	4.247(2)	4.849(2)	3.174(3)	3.334(2)	4.313(2)
O(1*e*)	116.18(8)	2.391(2)	3.279(3)	4.661(2)	3.862(2)	3.686(3)
O(1*f*)	152.53(7)	86.84(7)	2.380(2)	3.498(2)	3.482(2)	3.636(3)
O(2*a*)	77.11(7)	146.21(8)	92.02(7)	2.480(2)	4.425(2)	2.515(2)
O(4*e*)	77.13(5)	97.57(7)	85.50(6)	116.02(6)	2.734(2)	5.525(0)
O(4*g*)	105.36(6)	89.86(7)	88.53(7)	56.35(5)	170.18(8)	2.811(2)

$Na(3)O_6$ polyhedron

Na(3)	O(W)	O(2*c*)	O(2*h*)	O(3*a*)	O(3*h*)	O(4*d*)
O(W)	2.495(2)	3.340(3)	3.340(3)	3.346(2)	4.796(3)	3.334(2)
O(2*c*)	84.76(6)	2.460(2)	3.618(3)	2.513(2)	3.501(2)	4.852(2)
O(2*h*)	85.92(6)	96.07(7)	2.405(2)	4.719(2)	3.088(2)	3.381(2)
O(3*a*)	86.05(5)	62.17(6)	157.42(7)	2.407(2)	3.755(2)	3.981(2)
O(3*a*)	166.95(7)	93.82(7)	81.32(7)	104.77(6)	2.333(2)	3.556(2)
O(4*d*)	85.50(6)	168.64(7)	89.05(6)	111.30(7)	96.98(7)	2.416(2)

TABLE V

Hydrogen Bond Scheme (Angles and Distances)

O(W)–H	H. . . . .O(3)	O(W)–O(3)	H–O(W)–H	O(W)–H. . . .O(3)
(2×) 0.88(4) Å	(2×) 1.87(4) Å	2.732(2) Å	106(5)°	166(4)°

TABLE VI

Symmetry Code Used in Tables III and IV

x, y, z	(*a*)	$x, \bar{y}, \frac{1}{2} + z$	(*e*)
$\bar{x}, \bar{y}, \bar{z}$	(*b*)	$\bar{x}, y, \frac{1}{2} - z$	(*f*)
$\frac{1}{2} + x, \frac{1}{2} + y, z$	(*c*)	$\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$	(*g*)
$\frac{1}{2} - x, \frac{1}{2} - y, \bar{z}$		$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$	(*h*)

molecule located on a twofold axis. Table II gives the anisotropic thermal factors for the nonhydrogen atoms.

A unitary weighting scheme was used for all least-squares calculations.

Description of the Structure

The PO_4 tetrahedron, whose main interatomic distances and bond angles are re-

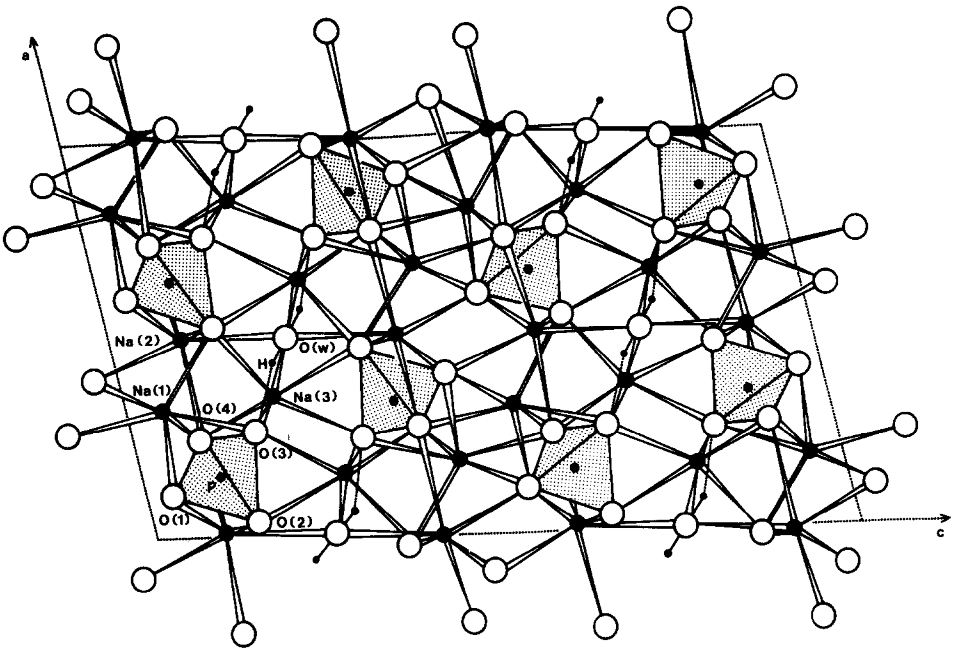

FIG. 1. Projection of the atomic arrangement along the **b** axis.

ported in Table III, is not very distorted:

$$1.533 < \text{P–O} < 1.544\ \text{Å},$$
$$108.23 < \widehat{\text{O–P–O}} < 110.24°,$$

with averages $\overline{\text{P–O}} = 1.540$ Å and $\widehat{\text{O–P–O}} = 109.47°$.

NaO_6 polyhedra. The three independent sodium atoms have a strongly distorted octahedral coordination. The main geometrical features of these polyhedra are reported in Table IV.

The water molecule and the hydrogen bond scheme. The water molecule is located on a twofold axis. Table IV reports the main characteristics for this molecule and the hydrogen bond scheme.

As can be seen from Fig. 1, this atomic arrangement may be described as a three-dimensional network of very distorted NaO_6 octahedra.

In addition, it may be noticed that NaO_6 octahedra are not equivalent. $Na(1)O_6$ polyhedron is built up only with oxygen atoms, while $Na(2)O_6$ and $Na(3)O_6$ polyhedra have a water molecule in their coordination. The average values for the Na–O distances in these three octahedra are, respectively, 2.439 (Na_1), 2.568 (Na_2), and 2.419 (Na_3).

References

1. J. D'ANS AND O. SCHNEINER, *Z. Phys. Chem.* **75**, 101 (1910).
2. H. MENZEL AND E. VON SAHR, *Z. Elektrochem.* **43**, 104 (1937).
3. O. T. QUIMBY, *Chem. Rev.* **40**, 147 (1974).
4. B. WENDROW AND K. A. KOBE, *Ind. Eng. Chem.* **44**, 1439 (1952).