

Preparation and Crystal Structure of $\text{Na}_3\text{SbO}(\text{PO}_4)_2$

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The single phase compound $\text{Na}_3\text{SbO}(\text{PO}_4)_2$ was prepared by a solid state reaction. It crystallizes in the orthorhombic system, space group $P2_12_12_1$, with $a = 6.964(1) \text{ \AA}$, $b = 9.284(2) \text{ \AA}$, $c = 12.425(2) \text{ \AA}$, $Z = 4$. The structure was determined from 968 reflections collected on a Nonius CAD4 automatic diffractometer with $\text{MoK}\alpha$ radiation. The final R index and weighted R_w index are 0.031 and 0.039, respectively. The structure is built up from strings of corner-sharing SbO_6 octahedra to which phosphate groups are linked by two of their vertices. These chains, running parallel to the a -axis, are separated from each other by sodium atoms. © 1991 Academic Press, Inc.

Introduction

Within a research program devoted to compounds likely to exhibit fast alkali-ion mobility, several phases which have been identified in the $\text{K}_2\text{O}-\text{Sb}_2\text{O}_5-\text{P}_2\text{O}_5$ system (1-3) can be ion-exchanged in acidic medium, thus leading to phosphato-antimonic acids which are ionexchangers, protonic conductors, and catalysts (4-6). Extending our investigations to other alkali ions, we prepared the $\text{Na}_3\text{SbO}(\text{PO}_4)_2$ compound. We report here on the refinement and description of its crystal structure.

Experimental

Single crystals of $\text{Na}_3\text{SbO}(\text{PO}_4)_2$ were grown from mixtures of NaNO_3 , Sb_2O_3 ,

and $\text{NH}_4\text{H}_2\text{PO}_4$ (all GR grade, Merck). The chemicals were weighed out in the stoichiometric ratio and the mixture was heated in a platinum crucible at 473 K for 4 hr to decompose the $\text{NH}_4\text{H}_2\text{PO}_4$ before calcining at 1073 K for 12 hr in air. The crystals obtained are colorless thin needles elongated in the [100] direction. Their chemical analysis, conducted with an electron microprobe, leads to an atomic Na: Sb: P ratio of 3:1:2. Single crystal X-ray study indicates that the compound is of orthorhombic symmetry. The cell parameters (Table I) were least-squares refined from powder diffraction data collected with an INEL curved multidetector, using a 0.2-mm capillary and $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54059 \text{ \AA}$; silicon as standard). The powder pattern (Table II) includes observed and calculated interplanar distances of the reflection planes along with the intensities calculated from the LAZY-

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TABLE I
CRYSTALLOGRAPHIC AND EXPERIMENTAL DATA

Crystal data	
Formula weight (g)	396.7
<i>a</i> (Å)	6.964(1)
<i>b</i> (Å)	9.284(2)
<i>c</i> (Å)	12.425(2)
<i>V</i> (Å ³)	803.4(4)
<i>Z</i>	4
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>D</i> _{calc} (g · cm ⁻³)	3.28
μ (MoK α)(cm ⁻¹)	40.31
Intensity measurement	
Crystal size (mm)	0.18 × 0.03 × 0.03
Radiation (Å)	MoK α , λ = 0.71069
Scan mode	ω
Scan angle (°)	$\Delta\omega$ = 1.0 + 0.35 tan θ
Recording angular angle (θ°)	1.5 – 30.0
Number of independent data observed with $\sigma(I)/I < 0.33$ used in refinements	968
Structure solution and refinement	
Number of variables (isotropic temperature factors)	62
$R = \frac{\sum (F_o - F_c)}{\sum F_o }$	0.047
$R_w = \frac{[\sum w(F_o - F_c)^2 / \sum w F_o^{-2}]^{1/2}}{\text{with } w = 1/(1 + [(F_{\text{obs}} - F_w)/F_{\text{max}}]^2)}$	0.059
Number of variables (anisotropic temperature factors)	92
<i>R</i> =	0.031
<i>R</i> _w =	0.039
Extinction parameter refined <i>g</i> =	2.4(3) × 10 ⁻⁷

PULVERIX program (7). Intensity data were collected with a Nonius CAD4 diffractometer operating under the conditions given in Table I. For the data reduction, structure solution, and refinement, the SDP-PLUS program chain (1982 version) of Enraf-Nonius, written by Frenz (8), was used. Because of the low value of the calculated linear absorption coefficient ($\mu = 40.31 \text{ cm}^{-1}$) and the crystal size, no absorption correction was applied.

Structure Determination

The positional parameters for the anti-mony atoms were determined from the three-dimensional Patterson map, with the remaining atoms being found from successive difference Fourier maps. Refinement was carried out by the full-matrix least-

squares method. In a preliminary stage of refinement the positional parameters and isotropic temperature factors were refined to $R = 0.047$ and $R_w = 0.059$. Then anisotropic temperature factors were assigned to all but oxygen atoms. The final stage of refinement with corrections for secondary extinction and anomalous dispersion converged to final $R = 0.031$ and $R_w = 0.039$. A refinement of the enantiomorph did not give a different R value. The final Fourier difference map is featureless with maxima and minima in the range $\pm 1.0 e \cdot \text{\AA}^{-3}$. Table III presents the final atomic coordinates and thermal parameters (structure factor tables will be sent upon request).

Description and Discussion of the Structure

In the structure of Na₃SbO(PO₄)₂, the SbO₆ octahedra and PO₄ tetrahedra are arranged in infinite chains running parallel to the *a*-axis.

In a chain, two consecutive octahedra, lying at $x \approx 0$ and $\frac{1}{2}$, are linked together via corner sharing and by the edge of two tetrahedra of different types. This arrangement of polyhedra forms a somewhat staggered string of SbO₆ octahedra with a Sb–O–Sb angle of about 128° (Fig. 1). Therefore each SbO₆ octahedron is connected to two other octahedra via opposite vertices and to four PO₄ tetrahedra (2 P(1)O₄ and 2 P(2)O₄). Two tetrahedra of the same type are linked to opposite vertices of a given octahedron. They lie at $x = \frac{1}{4}$ and $x = -\frac{1}{4}$, so that each of them connects this octahedron to one of its two adjacent neighbors at two different levels (Fig. 1). Then each PO₄ tetrahedron shares two vertices, with two consecutive octahedra in the chain and has two unshared vertices, i.e., not linked to the anti-mony atom. Each SbO(PO₄)₂³⁻ chain is surrounded by four identical chains at a distance of 7.8 Å (Fig. 2). This arrangement

TABLE II
X-RAY POWDER DIFFRACTION DATA (REFLECTIONS WITH $I/I_0 < 2$ HAVE BEEN OMITTED)

hkl	$d_{\text{obs}}(\text{\AA})$	$d_{\text{calc}}(\text{\AA})$	I/I_0	hkl	$d_{\text{obs}}(\text{\AA})$	$d_{\text{calc}}(\text{\AA})$	I/I_0
0 1 1	7.440	7.437	100	0 4 0	2.320	2.321	6
0 0 2	6.210	6.212	31	2 0 4		2.318	2
1 1 1	5.076	5.083	3	2 3 1	2.272	2.274	3
0 2 0	4.630	4.642	10	1 1 5		2.269	3
1 0 2		4.636	7	0 4 2	2.174	2.174	6
0 2 1	4.344	4.348	4	2 2 4		2.074	3
1 1 2	4.141	4.147	3	0 0 6	2.072	2.071	8
0 1 3	3.777	3.782	15	2 3 3	2.020	2.020	3
0 2 2	3.716	3.719	7	2 1 5	1.977	1.976	11
1 2 2	3.279	3.280	4	2 4 0		1.931	3
2 1 1	3.154	3.154	50	0 4 4		1.859	3
0 0 4	3.108	3.106	10	2 4 2	1.845	1.844	4
2 0 2	3.038	3.037	14	0 5 1		1.836	2
0 3 1	3.005	3.003	21	2 0 6		1.780	2
0 1 4	2.947	2.946	7	0 1 7	1.742	1.743	6
2 1 2	2.888	2.887	5	4 0 0		1.741	3
1 2 3		2.825	2	4 1 1	1.695	1.695	11
1 3 0	2.831	2.828	7	0 5 3		1.694	3
2 2 0	2.788	2.786	14	2 3 5		1.693	4
2 2 1	2.718	2.718	3	2 2 6	1.662	1.662	3
0 2 4	2.582	2.582	7	2 4 4		1.640	4
2 1 3	2.562	2.562	15	2 5 1	1.625	1.624	6
2 2 2	2.543	2.542	10	4 2 2	1.576	1.577	2
0 3 3	2.481	2.479	3	2 1 7	1.558	1.559	4
0 1 5	2.400	2.400	5				

TABLE IIIa
FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS

Atom	Position	x	y	z	$B(\text{\AA}^2)$
Sb(1)	4a	0.02103(6)	0.2463(1)	0.00476(5)	0.682(5) ^a
P(1)	4a	0.2629 (4)	0.5298(3)	0.9218 (2)	0.85 (4) ^a
P(2)	4a	0.7705 (4)	0.3749(3)	0.2004 (2)	0.85 (3) ^a
Na(1)	4a	0.7554 (7)	0.5866(4)	0.9833 (3)	1.64 (8) ^a
Na(2)	4a	0.3258 (8)	0.2425(6)	0.2600 (4)	2.83 (9) ^a
Na(3)	4a	0.3761 (7)	0.3934(6)	0.6594 (4)	2.13 (9) ^a
O(1)	4a	0.712 (1)	0.4690(8)	0.6686 (6)	1.1 (1)
O(2)	4a	0.4079 (9)	0.5486(7)	0.4850 (6)	1.1 (1)
O(3)	4a	0.451 (1)	0.4553(8)	0.9691 (6)	1.2 (1)
O(4)	4a	0.726 (1)	0.6968(8)	0.4444 (5)	0.89 (9)
O(5)	4a	0.588 (1)	0.3046(8)	0.1439 (6)	1.2 (1)
O(6)	4a	0.755 (1)	0.3374(8)	0.3169 (6)	1.4 (1)
O(7)	4a	0.255 (1)	0.4907(8)	0.3026 (6)	1.6 (1)
O(8)	4a	0.241 (1)	0.3181(9)	0.4605 (7)	1.9 (1)
O(9)	4a	0.548 (1)	0.7100(8)	0.6549 (6)	1.1 (1)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:

$$B_{\text{eq}} = 4/3 \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j.$$

TABLE IIIb
ANISOTROPICAL THERMAL PARAMETERS FOR THE ATOMS OF Na₃SbO(PO₃)₂ (Å² × 10³)

Atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Sb	4.6(1)	10.5(1)	10.9(2)	0.0(3)	0.4(2)	-0.3(3)
P(1)	6.6(9)	10.4(9)	15(1)	-0.4(9)	1.0(9)	2.0(9)
P(2)	9.4(9)	13.0(9)	9.7(9)	-0.6(9)	-0.2(9)	-0.6(9)
Na(1)	27(2)	18(2)	17(2)	-3(2)	0(2)	5(1)
Na(2)	55(3)	22(2)	30(2)	-14(3)	21(2)	-9(3)
Na(3)	25(2)	29(2)	26(2)	-8(2)	4(2)	0(2)

Note. The form of the anisotropic thermal parameter is:

$$\exp [-2\pi^2 (h^2a^*U_{11} + k^2b^*U_{22} + l^2c^*U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})].$$

TABLE IV
SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) FOR THE COORDINATION POLYHEDRA
(DIAGONAL O-O DISTANCES IN THE SbO₆ OCTAHEDRON HAVE BEEN OMITTED)

Sb(1)O ₆ octahedron						
Sb(1)	O(2 ⁱ)	O(3 ⁱⁱ)	O(4 ⁱ)	O(4 ⁱⁱⁱ)	O(5 ^{iv})	O(9 ^v)
O(2 ⁱ)	1.983(7)		2.66 (1)	2.82 (1)	2.87 (1)	2.77(1)
O(3 ⁱⁱ)	177.6(3)	1.962(8)	2.90 (1)	2.67 (1)	2.75 (1)	2.75 (1)
O(4 ⁱ)	85.0 (3)	95.8 (3)	1.950(7)		2.80 (1)	2.896(9)
O(4 ⁱⁱⁱ)	92.4 (3)	86.9 (3)	175.8(2)	1.927(7)	2.64 (1)	2.70 (1)
O(5 ^{iv})	93.2 (3)	89.2 (3)	85.0 (3)	91.9 (3)	1.964(7)	
O(9 ^v)	88.9 (3)	88.8 (3)	95.3 (3)	87.9 (3)	177.9(3)	1.970(7)
P(1)O ₄ tetrahedron						
P(1)	O(2 ^v)		O(3 ^v)		O(7 ^v)	O(8 ^v)
O(2 ^v)	1.601(7)		2.50 (1)		2.56 (1)	2.45 (1)
O(3 ^v)	103.4(3)		1.591(8)		2.57 (1)	2.49 (1)
O(7 ^v)	111.4(4)		112.3(4)		1.499(8)	2.54 (1)
O(8 ^v)	104.9(4)		108.0(5)		116.0(5)	1.492(9)
P(2)O ₄ tetrahedron						
P(2)	O(1 ^{vi})		O(5)		O(6)	O(9 ^{vi})
O(1 ^{vi})	1.507(8)		2.54 (1)		2.58 (1)	2.52 (1)
O(5)	110.1(4)		1.591(8)		2.46 (1)	2.54 (1)
O(6)	118.9(4)		105.9(3)		1.493(8)	2.47 (1)
O(9 ^{vi})	108.6(4)		105.9(3)		106.6(4)	1.591(7)
Na-O distances < 2.5 Å						
	Na(1)-O(1)				2.371(8)	
	Na(1)-O(3)				2.454(9)	
	Na(1)-O(6)				2.186(8)	
	Na(1)-O(8)				2.260(9)	
	Na(2)-O(1)				2.296(9)	
	Na(2)-O(5)				2.398(9)	
	Na(2)-O(7)				2.41 (1)	
	Na(3)-O(1)				2.445(9)	
	Na(3)-O(6)				2.321(9)	
	Na(3)-O(7)				2.27 (1)	

Note. The symmetry code is

i: $\bar{x} + 1/2; \bar{y} + 1; z - 1/2$

iii: $\bar{x} + 3/2; \bar{y} - 1/2; \bar{z}$

v: $\bar{x} + 1/2; \bar{y} + 1; z + 1/2$

ii: $\bar{x} - 1; y + 1/2; \bar{z} + 3/2$

iv: $\bar{x} - 1; y + 1/2; \bar{z} + 1/2$

vi: $\bar{x} + 3/2; \bar{y} + 1; \bar{z} - 1/2$

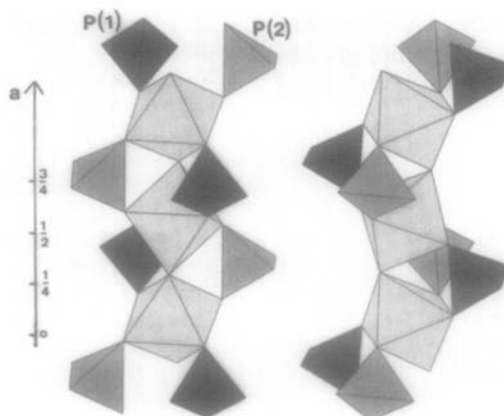


Fig. 1. $[011]^*$ view of two neighboring chains $\text{SbO}(\text{PO}_4)_2^-$.

of chains delimits three different crystallographic sites for the sodium ions.

Among the alkali phosphoantimonates already mentioned, $\text{Na}_3\text{SbO}(\text{PO}_4)_2$ is the second example of structure with a 1D covalent moiety. In the first one, K_2SbPO_6 (9), each PO_4 tetrahedron is linked to a string of edge sharing octahedra via two of its vertices and has two unshared oxygen atoms.

A list of bond distances and bond angles along with their standard deviations is

given for $\text{Na}_3\text{SbO}(\text{PO}_4)_2$ in Table IV. It can be seen from this table that all distances are reasonable and in good agreement with previous knowledge of phosphates and antimony(V) structural chemistry. The SbO_6 octahedron is slightly distorted with $\text{Sb}-\text{O}$ distances ranging from 1.927(7) Å to 1.983(7) Å. The two unshared oxygen atoms of the phosphate groups form two $\text{P}-\text{O}$ bonds significantly shorter (~ 1.50 Å) than the two others (~ 1.60 Å). This difference

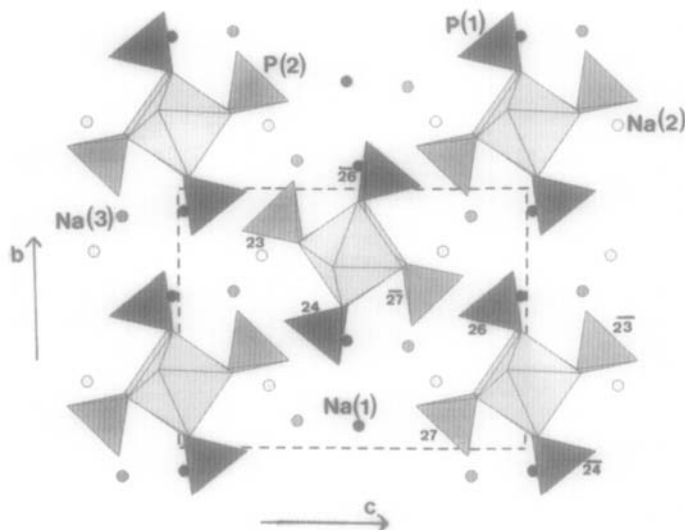


Fig. 2. $\text{Na}_3\text{SbO}(\text{PO}_4)_2$: projection of the structure on the b - c plane.

between P–O distances of shared or unshared oxygen atoms has been already observed in $K_3Sb_3P_2O_{14}$ (1), $KSbP_2O_8$ (2), and K_2SbPO_6 (9).

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