

## The Crystal Structure of $\text{SbPO}_4$

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The crystal structure of antimony phosphate has been determined from three-dimensional X-ray intensity data ( $\text{MoK}\alpha$ ) and refined to a final  $R$  value of 7.4 % (856 independent reflections). The crystals are monoclinic (space group  $P2_1/m$ ).

As for most other  $\text{Sb(III)}$  oxygen compounds antimony has a onesided coordination to four oxygen atoms with  $\text{Sb}-\text{O}$  distances between 1.98 and 2.19 Å. The structure is a layer structure with infinite sheets of composition  $\text{SbPO}_4$  extending parallel to the  $bc$  plane. Like lead in tetragonal  $\text{PbO}$  the antimony atoms form the outermost parts of the layers. The antimony atoms of different layers face each other without any shielding by oxygen atoms. The  $\text{SbPO}_4$  sheets are built up of  $\text{PO}_4$  tetrahedra and  $\text{SbO}_4$  polyhedra. Only corners are shared, and in this way each  $\text{SbO}_4$  polyhedron is in contact with four separate  $\text{PO}_4$  tetrahedra and each  $\text{PO}_4$  tetrahedron with four  $\text{SbO}_4$  polyhedra.

Solid antimony trioxide reacts with dilute acids forming basic salts in most cases. As part of a study on these reactions, the interaction between  $\text{Sb}_2\text{O}_3(\text{s})$  and  $\text{H}_3\text{PO}_4$  (0.5–6 M) was investigated. From powder photographs and chemical analyses it was found that the reaction product was  $\text{SbPO}_4$ , a result in agreement with that previously given by Robbins.<sup>1</sup>

### PREPARATION AND ANALYSIS

Solid  $\text{Sb}_2\text{O}_3$  was rotated with an excess of 6 M  $\text{H}_3\text{PO}_4$  at room temperature for one month. The suspension was then filtered through a glass filter funnel, washed thoroughly with cold water and dried at 120°C. The sample obtained in this way was micro-crystalline. In order to obtain single crystals large enough for X-ray work, the powder was heated for about 8 h in a platinum crucible at 800°C. The resulting product contained crystals of at least two different phases, but it was possible to pick out tiny, colourless single crystals of the parent substance  $\text{SbPO}_4$ .

After the homogeneity of the micro-crystalline  $\text{SbPO}_4$  powder was checked by Guinier powder photographs, the sample was analysed. To determine the antimony content, the compound was dissolved in hot concentrated  $\text{H}_2\text{SO}_4$ . The solution was diluted, heated and titrated with a  $\text{KBrO}_3$ -solution using methyl orange as indicator. The phosphorus

was determined spectrophotometrically as phosphovanadomolybdate. The results of the analyses were in agreement with the values calculated for  $\text{SbPO}_4$ : Sb (%) found  $56.4 \pm 0.5$ , calc. 56.2. P (%) found  $14.9 \pm 0.1$ , calc. 14.3.

#### SINGLE-CRYSTAL WORK AND DATA REDUCTION

A crystal with the dimensions  $0.024 \times 0.073 \times 0.155 \text{ mm}^3$  was used for the X-ray diffraction work. The reflections  $hk0$  to  $hk9$  were registered by integrated Weissenberg photographs. The radiation was Zr-filtered  $\text{MoK}\alpha$  radiation. The multi-film (3 films) technique was used, the films interleaved with steel foils of 0.005 cm thickness. The intensities of the integrated spots were determined by means of a micro densitometer.

For  $\text{SbPO}_4$  the calculated linear absorption coefficient  $\mu$  is  $90 \text{ cm}^{-1}$  and as the crystal was quite small, and the rotation axis was 0.155 mm, no absorption correction was applied. Corrections for the Lorentz and polarisation effects were performed in the usual way.

#### STRUCTURE DETERMINATION

*Unit cell and space group.* Powder photographs were taken in a Guinier-Hägg focussing camera with potassium chloride as internal standard and with strictly monochromatized  $\text{CuK}\alpha$  radiation. These photographs could be interpreted by a monoclinic unit cell, with the cell data obtained from the Weissenberg photographs. Refinements of the cell parameters were performed by the method of least squares, giving the following results:  $a = 5.0868 \pm 0.0006 \text{ \AA}$ ,  $b = 6.7547 \pm 0.0007 \text{ \AA}$ ,  $c = 4.7247 \pm 0.0005 \text{ \AA}$ ,  $\beta = 94.66 \pm 0.01^\circ$ ,  $V = 161.80 \pm 0.03 \text{ \AA}^3$ .

The observed density,  $4.3 \text{ g cm}^{-3}$ , is in fair agreement with the calculated value of  $4.45 \text{ g cm}^{-3}$  for two formula units  $\text{SbPO}_4$  per unit cell.

In addition to the intensity material collected with the crystal rotated around  $[001]$  ( $\text{MoK}\alpha$ ), the layer lines 0–4 around  $[010]$  were registered ( $\text{CuK}\alpha$ ). From these photographs the Laue symmetry was found to be  $2/m$ . The systematically absent reflections are  $0k0$  with  $k = 2n + 1$ , which is characteristic for the space groups  $P2_1/m$  (No. 11) and  $P2_1$  (No. 4).

*Positions of the atoms.* The positional parameters of the atoms were determined in the usual way, using in turn three-dimensional Patterson functions, electron density functions, and electron density difference syntheses (not given here). For these calculations the space group  $P2_1/m$  ( $b$  as unique axis) was assumed. The parameters obtained were refined by means of the method of least squares, using isotropic temperature factors for all atoms. After 5 cycles in the least-squares full-matrix refinement, the  $R$  factor was 7.4 % and the shifts in the parameters were negligible. Cruickshank's weighting scheme  $w = (a + |F_o| + c|F_o|^2 + d|F_o|^3)^{-1}$  with  $a = 35.0$ ,  $c = 0.005$  and  $d = 0$  was used in the calculations. The final positional parameters and temperature factors with their respective standard deviations are presented in Table 1. The weight analysis used in the last cycle of the refinements is given in Table 2, presenting

an overall view of the deviations  $||F_o|-|F_c||$  in the calculations. Lists of observed and calculated structure factors are not presented here, but will be sent upon request.

Table 1. Final fractional parameters and temperature factors and their standard deviations.

$P2_1/m$  ( $b$  as unique axis). 2 Sb, 2P, 2O<sub>1</sub>, 2O<sub>2</sub> in 2( $e$ ), 4O<sub>3</sub> in 4( $f$ ).

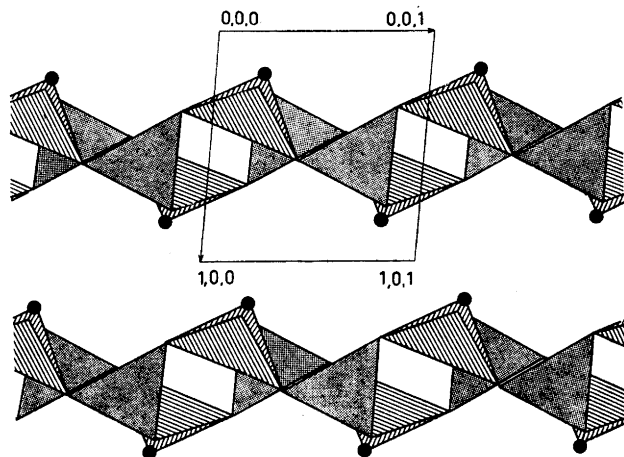
| Atom           | $x$    | $\sigma(x)$ | $y$           | $\sigma(y)$ | $z$    | $\sigma(z)$ | $B \text{ \AA}^2$ | $\sigma(B) \text{ \AA}^2$ |
|----------------|--------|-------------|---------------|-------------|--------|-------------|-------------------|---------------------------|
| Sb             | 0.1802 | 0.0002      | $\frac{1}{2}$ | —           | 0.2053 | 0.0002      | 0.43              | 0.02                      |
| P              | 0.6110 | 0.0007      | $\frac{1}{2}$ | —           | 0.7223 | 0.0007      | 0.36              | 0.04                      |
| O <sub>1</sub> | 0.3346 | 0.0022      | $\frac{1}{2}$ | —           | 0.8332 | 0.0021      | 0.65              | 0.12                      |
| O <sub>2</sub> | 0.5546 | 0.0024      | $\frac{1}{2}$ | —           | 0.3933 | 0.0025      | 0.85              | 0.13                      |
| O <sub>3</sub> | 0.7692 | 0.0019      | 0.0700        | 0.0015      | 0.8183 | 0.0022      | 1.33              | 0.12                      |

Table 2. Analysis of the weighting scheme used in the last cycle of the refinement. The intensity data were made up of 856 independent reflections.  $R=7.4\%$ .  $w$  is the weighting factor.  $\Delta = |F_o| - |F_c|$ .

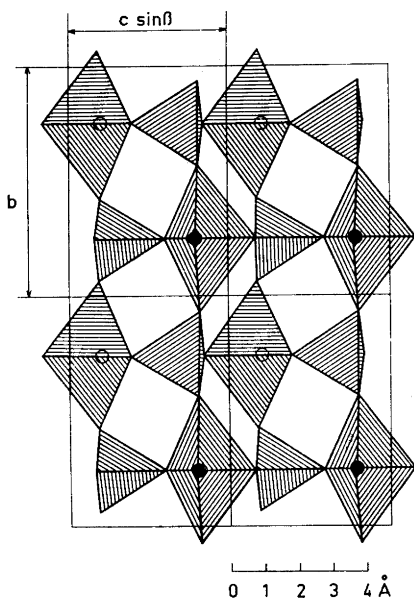
| Interval $\sin\theta$ | Number of independent reflections | $\overline{w\Delta^2}$ | Interval $ F_o $ | Number of independent reflections | $\overline{\Delta w^2}$ |
|-----------------------|-----------------------------------|------------------------|------------------|-----------------------------------|-------------------------|
| 0.00—0.38             | 207                               | 1.49                   | 0—17.7           | 85                                | 1.28                    |
| 0.38—0.48             | 182                               | 1.53                   | 17.7—20.6        | 86                                | 1.10                    |
| 0.48—0.55             | 144                               | 1.27                   | 20.6—22.9        | 85                                | 1.55                    |
| 0.55—0.60             | 111                               | 1.15                   | 22.9—25.2        | 85                                | 0.96                    |
| 0.60—0.65             | 82                                | 1.54                   | 25.2—27.8        | 86                                | 1.02                    |
| 0.65—0.69             | 52                                | 1.68                   | 27.8—30.8        | 86                                | 0.91                    |
| 0.69—0.73             | 41                                | 0.55                   | 30.8—34.6        | 85                                | 0.54                    |
| 0.73—0.76             | 26                                | 0.38                   | 34.6—38.8        | 86                                | 0.53                    |
| 0.76—0.79             | 7                                 | 0.39                   | 38.8—47.2        | 86                                | 0.92                    |
| 0.79—0.82             | 4                                 | 0.02                   | 47.2—116.3       | 86                                | 1.19                    |

Anisotropic temperature factors were then introduced for the antimony atoms and a slight improvement in the  $R$  factor from 7.4 to 6.8% resulted from a renewed least-squares calculation. Though these values (and also the weighted  $R$  factors) by themselves indicate that an anisotropic thermal motion exists for the antimony atoms, it must be borne in mind that no absorption correction was applied to the intensities. Therefore the author prefers to describe the thermal motions of all atoms in the unit cell with the aid of isotropic temperature factors.

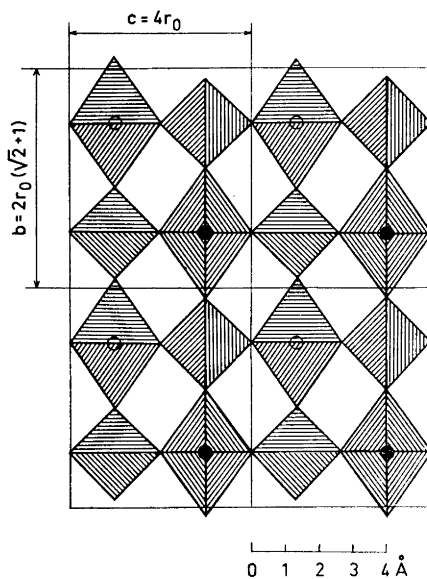
As the isotropic  $B$  values above do not show any large variation, and as the structure arrived at gives reasonable distances (*cf.* Table 3), it seems probable that the space group chosen ( $P2_1/m$ ) is the correct one. Positions in the polar space group  $P2_1$  were consequently not tried.



*Fig. 1a.* Projection of the structure of  $\text{SbPO}_4$  along the  $b$  axis on the  $ac$  plane. Several unit cells are drawn.  $\text{PO}_4$  tetrahedra and  $\text{SbO}_4$  polyhedra are indicated.



*Fig. 1b.* Projection of the structure along the  $a$  axis on the  $bc^*$  plane. Several unit cells are drawn.  $\text{PO}_4$  tetrahedra and  $\text{SbO}_4$  polyhedra are indicated. All oxygen atoms are indicated but only one layer  $\text{SbPO}_4$  is shown.



*Fig. 1c.* Projection of an idealized structure of  $\text{SbPO}_4$  on the  $bc$  plane. Several unit cells are shown.  $\text{PO}_4$  tetrahedra and  $\text{SbO}_4$  polyhedra are indicated.

Following the refinement, a total electron density difference synthesis was calculated to obtain a final test of the correctness of the structure ( $0 < x < 1$ ;  $0 < y < 0.25$ ;  $0 < z < 1$ ;  $\Delta x$ ,  $\Delta y$ , and  $\Delta z = 0.05$ ). For no point of this function did the calculated value amount to more than  $\pm 1/4$  of the height of an oxygen atom calculated with the same reflection material. This result seems to be satisfactory, bearing in mind that a photographic method of registration was used.

### DESCRIPTION OF THE STRUCTURE

The structure of  $\text{SbPO}_4$  is a layer structure in which infinite layers of composition  $\text{SbPO}_4$  extend parallel to the  $bc$  plane. The antimony atoms are unilaterally coordinated to four oxygen atoms.

*Geometrical aspects.* For the purpose of making comparisons with other known structures, the Sb—O configuration may be idealized in three ways:

1) The four oxygen atoms and the antimony atom form a *polyhedron with five corners*. The projections of the structure on the  $ac$  plane (Fig. 1a) and along the  $a$ -axis on the  $bc^*$  plane (Fig. 1b) are based on a coupling of such polyhedra with  $\text{PO}_4$  tetrahedra. It may be seen that only corners are shared. Every  $\text{SbO}_4$  polyhedron shares its four oxygen atom corners with four separate  $\text{PO}_4$  tetrahedra and every  $\text{PO}_4$  tetrahedron shares its four corners with four separate  $\text{SbO}_4$  polyhedra. In Fig. 1c a projection of an idealized structure of  $\text{SbPO}_4$  on the  $bc$  plane is given. In the idealized structure all short O—O edges of the polyhedra are supposed to be of equal length 2.67 Å. The mode of idealization will be obvious on comparing Figs. 1b and 1c.

2) The  $\text{SbO}_4$  polyhedron discussed above may be regarded as a *deformed tetrahedron* outside the longest edge of which the antimony atoms are situated. An idealized case would be an array of  $\text{MO}_4$  tetrahedra ( $M = \text{Sb}, \text{P}$ ) joined only by corners to endless sheets of composition  $\text{MO}_2$  (*cf.* Figs. 1b and 1c). However, no such structure is known to the author.

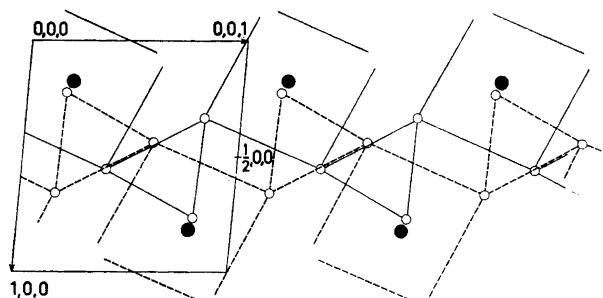


Fig. 2a. Projection of the structure of  $\text{SbPO}_4$  on the  $ac$  plane.  $\text{PO}_4$  tetrahedra and hypothetical  $\text{SbO}_4$  octahedra with two adjacent missing corners are indicated. Full lines indicate atoms at  $y = \frac{1}{4}$  and dashed lines atoms at  $y = \frac{3}{4}$ .

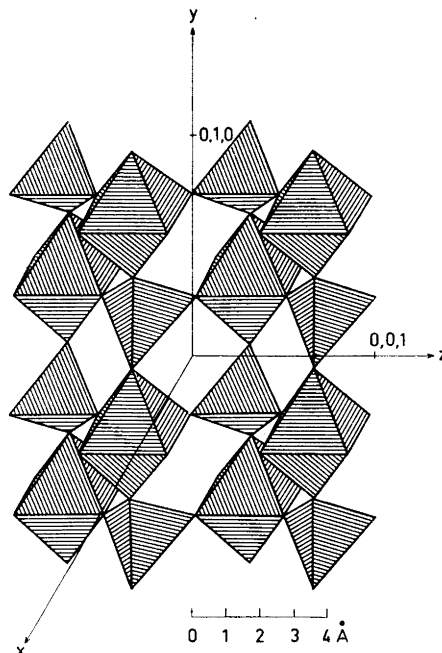


Fig. 2b. An idealized perspective picture of the coupling of hypothetical  $\text{SbO}_6$  octahedra and  $\text{PO}_4$  tetrahedra to an infinite layer parallel to the  $bc$  plane of the unit cell of  $\text{SbPO}_4$ . The positions of all oxygen atoms including the missing atoms are indicated.

3) The  $\text{Sb—O}$  configuration may be regarded as an octahedron with the antimony atoms in its center and with two adjacent oxygen atom corners missing. With this description each octahedron shares four corners with  $\text{PO}_4$  tetrahedra, while two adjacent corners do not take part. The structure of  $\text{SbPO}_4$  is visualized in this way in Fig. 2a (real structure, projection on the  $ac$  plane) and in Fig. 2b (idealized structure, perspective view of one layer  $\text{SbPO}_4$ ). According to these drawings one layer would have the general composition  $\text{ABO}_6$ , where A is octahedrally and B tetrahedrally coordinated. If the non-tetrahedral oxygen atoms (missing in the real structure  $\text{SbPO}_4$ ) are shared by an adjacent layer, the composition will be  $\text{ABO}_5$ . It was therefore reasonable to look for analogues among compounds  $\text{ABO}_5$  and  $\text{ABO}_6$ .

#### DISCUSSION

The crystal structures of  $\text{VOSO}_4$ ,<sup>2</sup>  $\text{MoOPO}_4$ ,<sup>3</sup> and  $\text{NbOPO}_4$ <sup>4</sup> are very much alike, being built up of  $\text{AO}_6$  octahedra and  $\text{BO}_4$  tetrahedra. In all of these structures the non-tetrahedral oxygen atoms correspond, however, to opposite shared corners of the  $\text{AO}_6$  octahedra. Thus the  $\text{M—PO}_4$  array is not the same in these structures as in  $\text{SbPO}_4$ . The three-dimensional network of the ion  $\text{MoO}_2\text{PO}_4^-$  in the structure of  $\text{Na}_2\text{MoO}_2\text{PO}_4$ <sup>5</sup> is, however, formally related to

the layers of  $\text{SbPO}_4$ . Every  $\text{MoO}_6$  octahedron has two adjacent non-shared oxygen atoms, corresponding to the missing corners in  $\text{SbPO}_4$ , while the rest of the oxygen atoms of the octahedron are shared by separate  $\text{PO}_4$  tetrahedra. Fig. 2a may be compared to Fig. 10 in Ref. 5. The arrangement of pairs of octahedra and pairs of tetrahedra around  $1/2, 0, 0$  in  $\text{NaMoO}_2\text{PO}_4$  is approximately the same as the corresponding arrangement around  $1/2, 0, 0$  in  $\text{SbPO}_4$  (cf. Fig. 2a). The repetition of these units is, however, different in the two structures leading to a layer structure for  $\text{SbPO}_4$  and to an infinite three-dimensional network for the ion  $\text{MoO}_2\text{PO}_4^-$  in  $\text{NaMoO}_2\text{PO}_4$ .

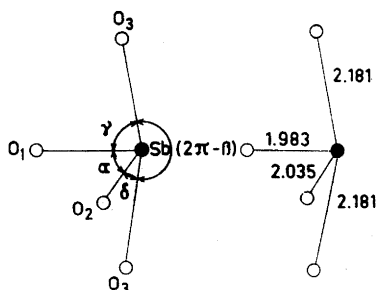


Fig. 3. Sb—O distances and notations for O—Sb—O angles in the  $\text{SbO}_4$  polyhedra in the structure of  $\text{SbPO}_4$ .

In  $\text{SbPO}_4$  the oxygen atoms lying close to antimony have Sb—O distances between 1.98 and 2.19 Å, while the next-nearest oxygen atoms are situated at a distance of 2.93 Å. The distances between oxygen atoms outside the  $\text{PO}_4$  tetrahedron are  $\geq 2.80 \pm 0.01$  Å. Notations and values of the angles O—Sb—O and the Sb—O distances are summarized in Fig. 3 and Table 3. In Table 3 a comparison of corresponding angles and distances in the related compounds  $\beta\text{-Sb}_2\text{O}_4$ <sup>6</sup> and  $\text{SbNbO}_4$ <sup>7</sup> is also given. There are no large differences between the values obtained for the three structures, and as seen from the angles the influence of the inert electron pair is apparent in all cases. The

Table 3. Sb—O distances (Å) and O—Sb—O angles (°) in the structures of  $\text{SbPO}_4$ ,  $\beta\text{-Sb}_2\text{O}_4$ , and  $\text{SbNbO}_4$  (cf. Fig. 3, Table 1).

|                      | $\text{SbPO}_4$ | $\beta\text{-Sb}_2\text{O}_4$ <sup>6</sup> | $\text{SbNbO}_4$ <sup>7</sup> |
|----------------------|-----------------|--|-------------------------------|
| Sb—O <sub>1</sub>    | 1.983 ± 0.010   | 2.032 ± 0.009                              | 2.008 ± 0.009                 |
| Sb—O <sub>2</sub>    | 2.035 ± 0.012   | 2.032 ± 0.009                              | 2.035 ± 0.009                 |
| Sb—O <sub>3</sub>    | 2.181 ± 0.010   | 2.218 ± 0.009                              | 2.134 ± 0.009                 |
| Sb—O <sub>3</sub> '  | 2.181 ± 0.010   | 2.218 ± 0.009                              | 2.331 ± 0.009                 |
| Sb—O <sub>3</sub> '' | 2.927 ± 0.010   | —  | 2.557 ± 0.009                 |
| α                    | 87.9 ± 0.5      | 87.9 ± 0.4                                 | 92.1 ± 0.4                    |
| β                    | 164.8 ± 0.5     | 148.1 ± 0.4                                | 150.7 ± 0.4                   |
| γ                    | 84.1 ± 0.3      | —  | —                             |
| δ                    | 85.0 ± 0.3      | —  | —                             |

SbPO<sub>4</sub> layers built up from PO<sub>4</sub> tetrahedra joined by antimony atoms are shown in Fig. 1b. The distances and angles within the PO<sub>4</sub> groups are normal; their values are given in Table 4.

Table 4. Distances (Å) and angles (°) within the PO<sub>4</sub> tetrahedron in the structure of SbPO<sub>4</sub>.

|                                    |               |
|------------------------------------|---------------|
| P—O <sub>1</sub>                   | 1.540 ± 0.011 |
| P—O <sub>2</sub>                   | 1.558 ± 0.012 |
| P—2 O <sub>3</sub>                 | 1.507 ± 0.010 |
| O—O                                | ≥ 2.44 ± 0.02 |
| ∠ O <sub>1</sub> —P—O <sub>2</sub> | 103.9 ± 0.6   |
| ∠ O <sub>1</sub> —P—O <sub>3</sub> | 112.2 ± 0.5   |
| ∠ O <sub>2</sub> —P—O <sub>3</sub> | 110.5 ± 0.5   |
| ∠ O <sub>3</sub> —P—O <sub>3</sub> | 107.5 ± 0.8   |

In the related compound monoclinic BiPO<sub>4</sub>,<sup>8</sup> the bismuth atoms are in contact with four PO<sub>4</sub> tetrahedra in the same way as antimony in SbPO<sub>4</sub>, but bismuth is coordinated with five oxygen atoms and the BiO<sub>5</sub> polyhedron shares *one edge* with one of the PO<sub>4</sub> tetrahedra. The Bi—O distances vary between 2.33 and 2.62 Å. In tetragonal BiAsO<sub>4</sub>,<sup>9</sup> the bismuth atom is in contact with eight separate PO<sub>4</sub> tetrahedra, thus coordinated to eight oxygen atoms in the form of a dodecahedron. The coordination is of the form 4+4, where the short Bi—4 O distances are 2.49 and the long ones 2.59 Å.

The antimony atoms in SbPO<sub>4</sub> are as mentioned above unilaterally coordinated to four oxygen atoms and in fact the antimony atoms represent the outermost parts of each respective layer (Fig. 1a). In this respect the structure has some resemblance to that of tetragonal PbO, where the metal atom also contains an inert electron pair.

*Acknowledgements.* The author wishes to thank Professor Bengt Aurivillius, The Lund Institute of Technology, for his never failing interest in this work, and for many valuable discussions during its performance, and Dr. Lennart Kinberger, University of Gothenburg, for an introduction to the field of X-ray crystallography. Preliminary work on the structure was performed under his guidance. Thanks are also due to the *Computer Division of the National Rationalization Agency* for providing free time on the CD 3600 computer in Uppsala.

These studies form part of a research program on salts of heavy metals, financially supported by the *Swedish Natural Science Research Council*.



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Received June 24, 1969.