# RAPID COMMUNICATION

# Synthesis and Structure of $Sb_5PO_{10}$, a New Phosphate of Antimony(III)

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The antimony(III) phosphate, $Sb_5PO_{10}$, is a framework structure built from vertex-sharing tetrahedral $Sb^{III}O_3E$ and trigonal bipyramidal $Sb^{III}O_4E$ moieties ($E$ = lone pair) and $P^VO_4$ tetrahedral units; orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 6.8373(5)$, $b = 7.0932(5)$, $c = 19.8730(15)$ Å, $V = 963.81(12)$ Å$^3$, $Z = 8$. The structure, determined by single crystal X-ray diffraction, is based on alternating layers of antimony oxide and antimony phosphate. © 2000 Academic Press

## INTRODUCTION

Nearly all framework structures containing antimony(III) oxide layers are built from sheets similar to those found in the orthorhombic form of $Sb_2O_3$ (1). Such systems include the single sheets of $SbNbO_4$ (2), $\alpha$-$Sb_2O_4$ (3), $\beta$-$Sb_2O_4$ (4), and the $Sb_n^{III}Sb_x^V(Ta^V,Nb^V)_{n-x}TiO_{4n+2}$ family (5), and the double sheets of $Sb_2MoO_6$ (6), $Sb_2VO_5$ (7), and $Sb_2W_{1-x}V_xO_{6-x}$ (8). During a systematic exploration of the $Sb_2O_3/P_2O_5$ system (9), we found an antimony-rich framework phosphate, $Sb_5PO_{10}$, that is constructed from novel antimony oxide and antimony phosphate layers.

## EXPERIMENTAL

$Sb_5PO_{10}$ was synthesized from a mixture of potassium antimonyl tartrate trihydrate (Aldrich), 85 wt.% phosphoric acid (Fisher), sodium hydroxide (Fisher), and water in a molar ratio of 1 Sb: 1.3 P: 1.0 Na: 350 $H_2O$. This was sealed in a PTFE-lined stainless steel autoclave and heated at 200°C under autogenous pressure for 3 days. The final pH of the solution was 4.3. The solid was filtered, washed with deionized water, and dried at 100°C in air. The product was pure (as determined by comparison of the powder X-ray diffraction pattern with the pattern simulated from the final

structure solution), consisting of rod-shaped crystals of $Sb_5PO_{10}$. The nature of the product is dependent upon the reaction temperature and the pH. After 3 days at 130°C, for example, the product consists of large crystals of recrystallized potassium antimonyl tartrate trihydrate. For $T = 200$°C, but a final pH $< 3$, the product is $SbPO_4$; for pH $> 6$, the product is a mixture of cubic and orthorhombic $Sb_2O_3$.

A single crystal of the title compound ($0.06 \times 0.05 \times 0.30$ mm) was glued to a thin glass fiber with cyanoacrylate (Superglue) adhesive. X-ray data were collected on a Siemens SMART CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo$K\alpha$ radiation, $\lambda = 0.71073$ Å) operating at 35 kV and 30 mA. About 1.3 hemispheres of intensity data were collected in 1321 frames with $\omega$ scans (width 0.30°, exposure time 30 s per frame). Unit cell constants were determined by a least-squares fit of 3696 reflections in the range $4° < 2\theta < 56°$. Crystal data: orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 6.8373(5)$, $b = 7.0932(5)$, $c = 19.8730(15)$ Å, $V = 963.81(12)$ Å$^3$, $Z = 8$, FW = 799.77 g mol$^{-1}$, $\rho_{calc} = 5.511$ g cm$^{-3}$. 5880 reflections were collected in the range $-8 \le h \le 8$, $-7 \le k \le 9$, $-25 \le l \le 26$, and merged to give 2152 unique reflections. The absorption correction was based on symmetry equivalent reflections using the SADABS (10) program; $R(int) = 0.0434$, $R(\sigma) = 0.0392$. The structure was solved by direct methods using SHELXS-97 (11) and difference Fourier syntheses. Full matrix least-squares structure refinement against $|F|^2$ was carried out using the SHELXTL-PLUS (11) package of programs. The last cycles of refinement included atomic positions and anisotropic thermal parameters for all atoms. The final Fourier map had minimum and maximum peaks of $-1.056$ and $1.199$ Å$^3$, respectively. Flack parameter $= 0.0089$, $R(int) = 0.0434$, $R(F) = 0.0263$, $R_w(F^2) = 0.0559$, and $S(F^2) = 1.032$ for 146 parameters (12).

## RESULTS AND DISCUSSION

A description of the $Sb^{III}$ coordination environment is dependent upon the definition of the $Sb^{III}$ bonding sphere (13). One approach defines this sphere as that containing the species at a distance, $r$, where the bond valence, $s$, is greater than $\sim 0.08$, where $s = \exp[(r_o - r)/b]$ ($r_o$ and $b$ are empirical parameters) (14). For $Sb^{3+}$ and $O^{2-}$, $r \approx 3.1$ Å (for $s \geq 0.08$), about equal to the sum of the van der Waals radii. Then the local coordination environment of $Sb^{3+}$ can be described in nearly all cases as a distorted octahedron, where (somewhat arbitrary) distinctions can be employed, such as "primary bonds" ($r \leq 2.4$ Å), "intermediate bonds" ($2.4$ Å $\leq r \leq 2.7$ Å), and "secondary bonds" ($2.7$ Å $\leq r \leq 3.1$ Å). It is the relatively wide range of acceptable Sb–$X$ bond distances (perfectly illustrated by the distribution of Sb–O distances in $Sb_5PO_{10}$ (Fig. 1)), and to a lesser extent, $X$–Sb–$Y$ bond angles, that allows $Sb^{3+}$ to adopt a variety of local geometries. The division between primary bonds and other interactions is clear for the title compound (Fig. 1) and, for clarity, only primary bonds are considered in the depiction of the local coordination spheres of the 16 independent atoms (Fig. 2). Atomic coordinates are given in Table 1; bond distances and angles for $[SbO_3E]$ tetrahedra, $[SbO_4E]$ trigonal bipyramids ($E$ = lone pair), and $[PO_4]$ tetrahedra agree with those found in reported antimony(III) phosphates (9, 15).

The title compound consists of alternating layers of antimony oxide and antimony phosphate (Fig. 3). The antimony phosphate layer is made of chains, identical to those found in $SbPO_4$, built from edge-sharing four-membered "$Sb_2P_2$" rings. In $SbPO_4$ these chains are connected to each other to form sheets, but in $Sb_5PO_{10}$ they connect to the antimony oxide layers. The antimony oxide layer is a double sheet.

For the related compound $Sb_2VO_5$, in which double sheets of antimony oxide are stacked between single sheets of vanadium oxide, the formula is sometimes written as $[Sb_2O_2]^{2+}[VO_3]^{2-}$ to emphasize the nature of the layers. If it is written as $[Sb_4O_4]^{4+}[V_2O_6]^{4-}$, and title compound as $[Sb_4O_5]^{2+}[SbOPO_4]^{2-}$ (the oxygen anions bridging two types of sheets are assigned to the vanadate or phos-

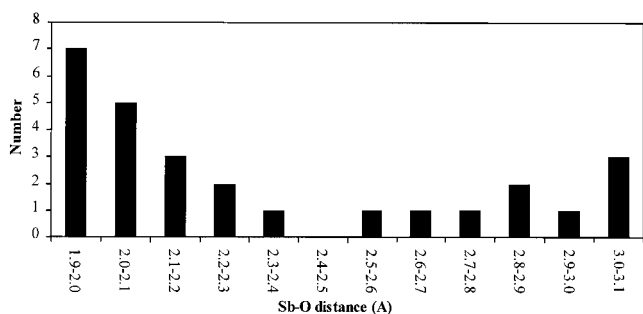phate sheet, respectively), comparison indicates the antimony oxide layer of the title compound to be relatively oxygen-rich; not surprisingly, the two have different volumes. The $[Sb_4O_4]^{4+}$ layer of $Sb_2VO_5$ contains two parallel sheets, with all $Sb^{3+}$ centers of each layer lying in the same plane. Adjacent $Sb^{3+}$ cations are out-of-plane with respect to each other in the $ab$ plane in the antimony oxide layer of the title compound (Fig. 3). However, undulating
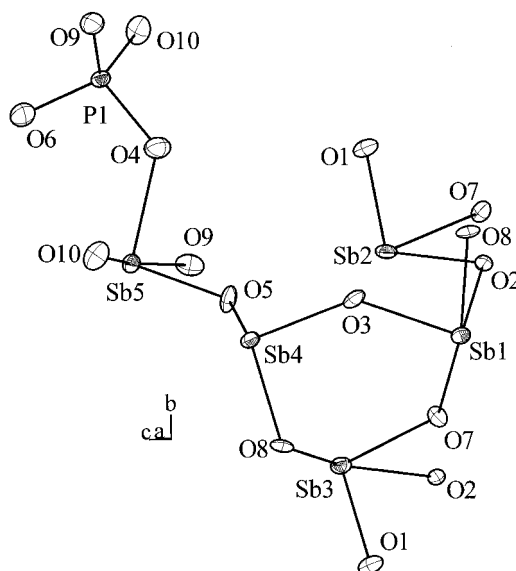
**FIG. 2.** The local coordination spheres of $Sb_5PO_{10}$. Thermal ellipsoids are given at 50% probability.

**FIG. 1.** The distribution of Sb–O distances in $Sb_5PO_{10}$.

**TABLE 1**
**Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å$^2$)**

| Atom | $x$ | $y$ | $z$ | $U$(eq) |
|------|------|------|------|---------|
| Sb1 | 0.62170(8) | 0.76828(8) | 0.81257(2) | 0.01198(13) |
| Sb2 | 0.90648(8) | 0.98549(8) | 0.69617(3) | 0.01266(13) |
| Sb3 | 1.14795(8) | 0.97275(8) | 0.84066(3) | 0.01271(13) |
| Sb4 | 0.59136(7) | 0.26468(8) | 0.85468(3) | 0.01120(12) |
| Sb5 | 0.38890(8) | 0.46301(8) | 1.00058(2) | 0.01260(13) |
| P1 | 0.4017(3) | 0.9064(3) | 1.02590(11) | 0.0116(4) |
| O1 | 0.7734(7) | 1.2297(9) | 0.6993(3) | 0.0144(12) |
| O2 | 0.8454(8) | 0.9490(8) | 0.7988(3) | 0.0115(12) |
| O3 | 0.5664(8) | 0.8612(8) | 0.7203(3) | 0.0141(13) |
| O4 | 0.3879(9) | 0.7376(8) | 0.9746(3) | 0.0205(13) |
| O5 | 0.3777(9) | 0.3714(8) | 0.9097(3) | 0.0159(13) |
| O6 | 0.4289(9) | 0.8243(9) | 1.0963(3) | 0.0208(14) |
| O7 | 0.8468(8) | 0.5827(8) | 0.7530(3) | 0.0133(13) |
| O8 | 0.4672(7) | 1.0129(8) | 0.8455(3) | 0.0118(11) |
| O9 | 0.0771(8) | 1.4666(8) | 0.9950(3) | 0.0181(12) |
| O10 | 0.2173(8) | 1.0268(10) | 1.0194(3) | 0.0199(14) |

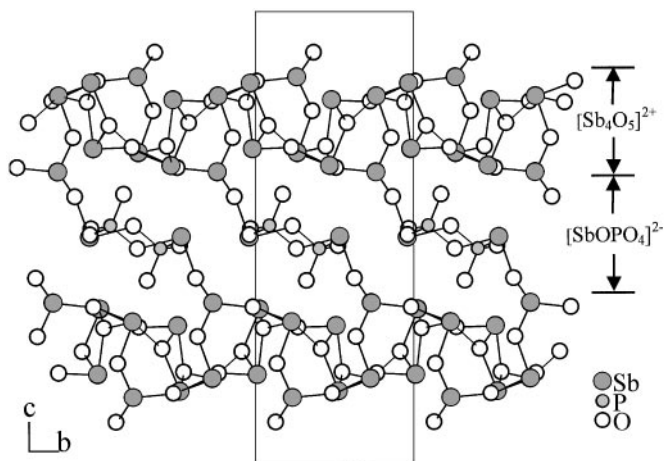*Note.* $U$(eq) is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

**FIG. 3.** $Sb_5PO_{10}$ viewed down the *a* axis. Only Sb–O bonds up to 2.4 A are shown for clarity.

sheets, viewed perpendicular to the *ab* plane, define almost the same area per $Sb^{3+}$ cation as the sheets of $Sb_2VO_5$ (Fig. 4). It is the greater separation between the sheets (4.161 Å in $[Sb_4O_5]^{2-}$ vs 3.191 Å in $[Sb_4O_4]^{4-}$, as measured between planes defined by the outermost $Sb^{3+}$ centers) that allows the layer of the title compound to accommodate extra oxygen anions while all antimony cations maintain a formal valence of $+3$ (Table 2).

Thermogravimetric analysis under flowing air at 5°C/min shows $Sb_5PO_{10}$ to be stable to $\sim 525°C$, when it begins to lose 30% of its weight; weight loss is complete by $\sim 800°C$. The powder X-ray diffraction of this product reveals a mixture of $\alpha$-$Sb_2O_4$ and $SbPO_4$. Both results agree with the loss of two Sb and one O atom per formula unit accompanied by the oxidation from $Sb^{3+}$ to $Sb^{5+}$ of one third of the remaining antimony cations.

The structure of $Sb_5PO_{10}$ demonstrates the adaptability of antimony(III) oxide sheets in forming novel frameworks, confirming the variety of antimony oxide sheets seen in *layered* antimony(III) oxides (16). Searches for new structures built from metal oxide layers interleaved with sheets of antimony(III) oxide then need not be constrained to those that have a particular arrangement of oxygen anions to match that of the bridging anions of the ubiquitous orthorhombic $Sb_2O_3$-type layers. This is significant, since some $Sb^{3+}$-containing oxides have been shown to be oxidation catalysts, most notably $\alpha$-$Sb_2O_4$, used commercially as a cocatalyst in the ammoxidation of propene to acrylonitrile (17). The few known $Sb^{3+}/Re^{7+}$ oxides are catalytically active in the oxidation of isobutylene to methacrolein, but their low thermal stability is discouraging (18). Substitution of $Re^{7+}$ for some of the $P^{5+}$ in the title compound (accompanied by the addition of $O^{2-}$ for charge compensation) could result in a more thermally stable oxidation catalyst.
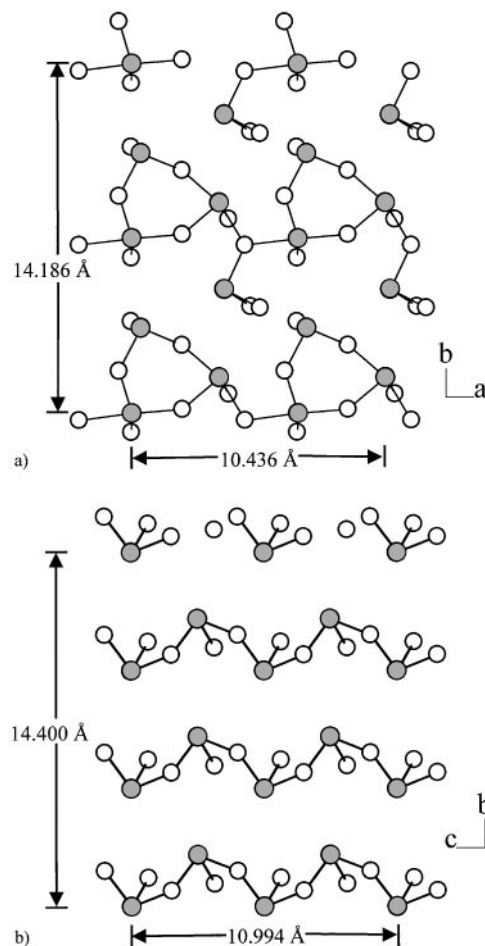


**FIG. 4.** The arrangement 18 $Sb^{3+}$ centers are depicted for each sheet of $Sb^{3+}$ cations in (a) $Sb_5PO_{10}$ and (b) $Sb_2VO_5$, showing that the projections of both sheets occupy nearly the same area.

Finally, we have examined the question as to whether the phase reported as $Bi_5PO_{10}$ (19), whose structure is unreported, is isostructural with the title compound. Comparing the unit cells, however, shows them to be apparently unrelated. An alternative possibility is that $Bi_5PO_{10}$ is

**TABLE 2**
**Calculated Valences of $Sb^{3+}$ Cations**

| Atom | S |
|------|------|
| Sb1 | 3.012 |
| Sb2 | 2.870 |
| Sb3 | 2.974 |
| Sb4 | 2.917 |
| Sb5 | 3.129 |

*Note.* The calculated valence of an individual ion, $S$, is the sum of the valences, $s$, of the surrounding bonds ($r \leq 3.1$ Å) calculated from the equation in the text. Sb5 belongs to the phosphate sheet.

actually $Bi_{12}P_2O_{23}$, whose unit cell is nearly identical to that of $Bi_5PO_{10}$ but whose structure is also unknown (20).

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