A Novel Framework Antimony (III) Phosphate: Synthesis and Structure of $NaSb_3O_2(PO_4)_2$

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The antimony (III) phosphate, $NaSb_3O_2(PO_4)_2$, is a framework structure built from Sb^{III} and P^V centers; orthorhombic, space group *Pca2₁* (No. 29), $a = 13.944(3)$, $b = 6.6822(13)$, $c = 20.886(4)$ Å, $V = 1946.1(7)$ Å^3, $Z = 8$. Stereochemically active lone pairs of electrons associated with $Sb^{III}O_5$ and $Sb^{III}O_4$ polyhedra point into eight-ring channels, approximately 5×7 Å^2, which dominate the architecture of the title compound. Charge-compensating sodium cations occupy the remaining space in the channels. © 2000 Academic Press

INTRODUCTION

Crystalline nanoporous aluminosilicates find extensive use as catalysts (particularly acid catalysts), adsorbents, molecular sieves, and ion exchangers (1). The report of a series of aluminophosphates in 1982 (2) stimulated the search for other open-framework metal phosphates. The next generation included those containing divalent transition metal cations (especially Co^{2+} and Zn^{2+}) that take up tetrahedral $[MO_4]$ coordination like the $[AlO_4]$, $[SiO_4]$, and $[PO_4]$ units of most zeolites and AlPO₄s. Since many of the properties of porous materials depend on their composition *and* architecture, recent attention has been paid to incorporating other main group and transition metals into open frameworks, and more materials are being reported that contain polyhedra such as $[XO_3]$, square pyramidal $[XO_4]$, and $[XO_6]$ units (3). A series of open-framework tin (II) phosphates (4) was recently synthesized, constructed from vertex-sharing trigonal pyramidal $[SnO_3]$ units (the lone pair of electrons of Sn^{II} presumably occupies the fourth corner of a quasi-tetrahedron) and tetrahedral $[PO_4]$ units, resulting in novel architectures. One of the materials (4*f*) exhibits porosity, having reversible dehydration and ion-exchange properties, and isolated Sn^{II} sites offer the possibility that redox or base catalyzed reactions may also occur. Sb^{III}, like Sn^{II}, has

a stereochemically active lone pair. While open frameworks based on Sb^{III} are known, including sulfides (5) and the mineral cetineite and related synthetic phases (6), almost all reported phosphates are either Sb^V (7) or mixed-valence Sb^{III}/Sb^V materials (8). With this in mind, we extended the search for novel *p*-block based phosphates into the Sb_2O_3/P_2O_5 system. To our knowledge, only two phosphates are based on Sb^{III}: condensed $SbPO_4$ (9) and layered $SbO(H_2PO_4) \cdot H_2O$ (10).

EXPERIMENTAL

$NaSb_3O_2(PO_4)_2$ was synthesized from a mixture of $SbCl_3$, 1,4-diaminobutane (DAB), phosphoric acid, sodium hydroxide, and water in a molar ratio of 1 Sb : 2.4 P : 1.2 Na : 1.5 DAB : 175 H_2O. This was sealed in a PTFE-lined stainless steel autoclave and heated at 135°C under autogenous pressure for two weeks. The solid was filtered, washed with deionized water, and dried at 100°C in air. The product consisted of (at least) three phases: about 10% was colorless, parallel-piped crystals of the title compound; a trace amount of Sb_2O_3, identified from powder X-ray diffraction; and the majority a layered material (11), $[H_3N(CH_2)_4NH_3]_{0.5} \cdot [SbO(HPO_4)]$, closely related to $SbO(H_2PO_4) \cdot H_2O$ (10). A single crystal ($0.04 \times 0.04 \times 0.45$ mm) of the title compound 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 45 kV and 35 mA. About 1.3 hemispheres of intensity data were collected in 1321 frames with ω scans (width 0.30°, exposure time 30 s per frame). Unit cell constants were determined by a least-squares fit of 6490 reflections (12) in the range $4° < 2\theta < 47°$. Crystal data: orthorhombic, space group *Pca2₁* (No. 29), $a = 13.944(3)$, $b = 6.6822(13)$, $c = 20.886(4)$ Å, $V = 1946.1(7)$ Å^3, $Z = 8$, FW = 610.18 g mol^{-1}, $\rho_{calc} = 4.165$ g cm^{-3}. There were 8979 reflections collected in the range $-15 \leq h \leq 15$, $-7 \leq k \leq 7$, $-17 \leq l \leq 23$ and merged
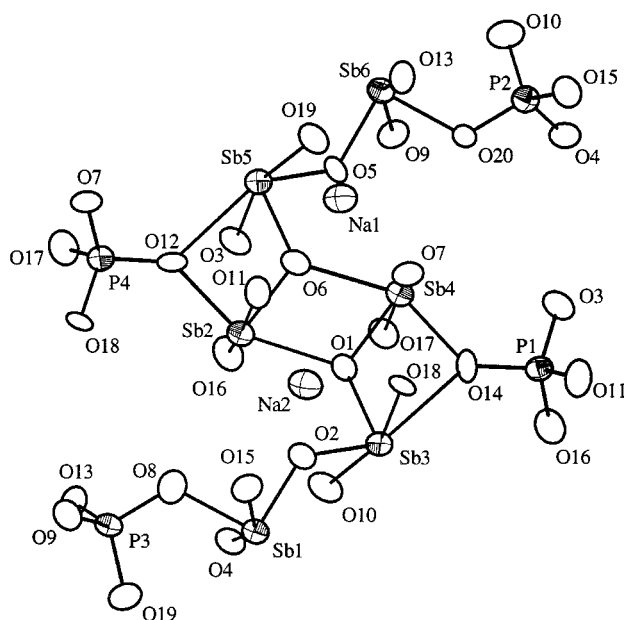
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FIG. 1. Asymmetric unit of $NaSb_3O_2(PO_4)_2$ (thermal ellipsoids are given at 50% probability). Four edge-sharing $[SbO_5]$ units and two $[PO_4]$ units result in four three-coordinated O atoms.

to give 2406 unique reflections ($R_{merg.} = 0.0608$). The absorption correction was based on symmetry equivalent reflections using the SADABS (12) program. The structure was solved by direct methods using SHELXS-97 (13) and difference Fourier syntheses. Full matrix least-squares structure refinement against $|F|^2$ was carried out using the

SHELXTL-PLUS (13) 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 -1.075 and 2.693 $Å^3$, respectively. Final $R(F) = 0.0399$, $R_w(F^2) = 0.1279$, and $S(F^2) = 1.211$ for 290 parameters and 2406 reflections (14). The structure displays local centers of symmetry, common to space group $Pca2_1$, as described by Marsh *et al.* (15). Elemental analysis performed on a Thermo Jarrell Ash IRIS inductively coupled plasma (ICP) spectrometer gave $Na/P = 0.49$ and $Sb/P = 1.51$ (atom basis), which agrees with the composition of the title compound.

RESULTS AND DISCUSSION

The asymmetric unit of $NaSb_3O_2(PO_4)_2$ has 32 independent atoms (Fig. 1); atomic coordinates are given in Table 1. The coordination sphere of antimony (III) often defies a simple description. Sb–O bonds can be described as (i) primary, consisting of bond distances (~ 2.1 Å) that are comparable to the sum of the covalent radii (16); (ii) secondary, with bond distances (~ 3.0 Å) that are a little shorter than the sum of the van der Waals radii (17); and (iii) intermediate, having distances (~ 2.6 Å) lying somewhere in between (i) and (ii) (18). These complexities are well described in two reviews (19). The local environment around each Sb^{III} center in $NaSb_3O_2(PO_4)_2$ is described below by accounting for the stereochemistry of the lone pair, primary, and intermediate bonds. Thus, the structure is built from four $[SbO_5]$ distorted ψ-octahedra, two $[SbO_4]$ ψ-trigonal
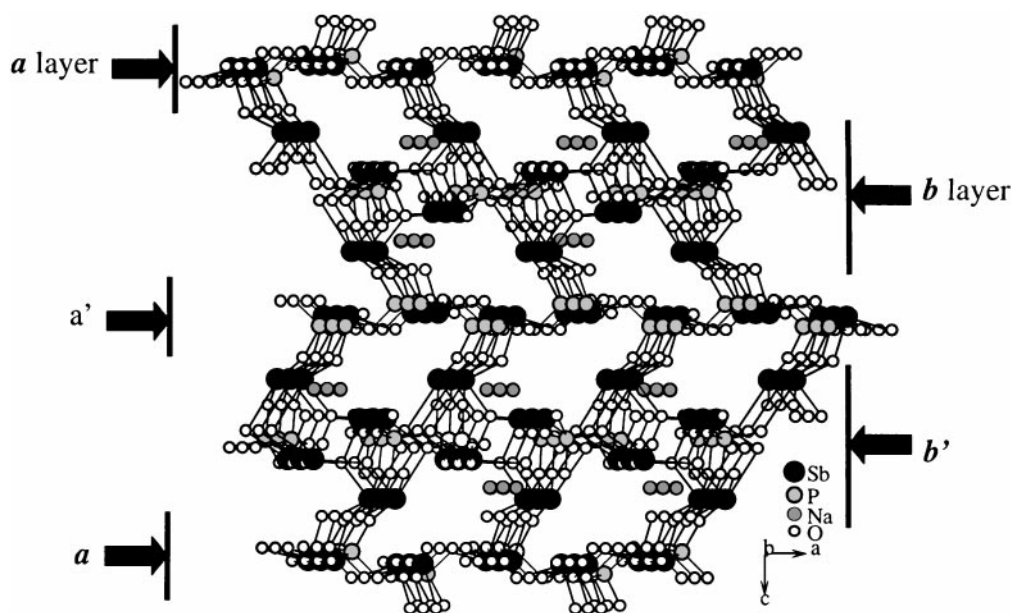

FIG. 2. The structure is described by the *abcd* stacking of **a**, **b**, **a′**, and **b′** layers, giving rise to eight-ring channels that run in the [010] direction.

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

Atom	x	y	z	U(eq)
Sb1	0.36050(9)	0.53593(18)	0.20949(6)	0.0301(4)
Sb2	0.23140(8)	0.29306(17)	0.50455(6)	0.0295(4)
Sb3	0.01210(8)	0.64130(17)	0.08508(7)	0.0290(4)
Sb4	0.51067(8)	0.78526(17)	0.42401(7)	0.0295(4)
Sb5	0.25813(9)	1.16103(17)	0.34376(7)	0.0295(4)
Sb6	0.10951(9)	0.99174(16)	0.21641(7)	0.0296(4)
P1	0.2796(3)	0.8087(7)	0.4657(2)	0.0277(14)
P2	−0.1058(3)	0.9650(7)	0.1906(3)	0.0300(14)
P3	0.1415(4)	0.4843(7)	0.2351(3)	0.0290(16)
P4	0.4636(3)	0.3028(7)	0.4627(3)	0.0283(16)
Na1	0.1281(6)	0.6990(12)	0.3652(4)	0.041(3)
Na2	0.3850(6)	0.8121(12)	0.0632(4)	0.042(3)
O1	0.5668(8)	0.7371(16)	0.5128(7)	0.027(3)
O2	−0.0967(8)	0.4995(17)	0.1217(8)	0.031(4)
O3	0.2737(10)	0.8748(18)	0.3951(7)	0.038(4)
O4	−0.1749(9)	0.7989(16)	0.2101(7)	0.033(4)
O5	0.1491(8)	1.011(2)	0.3068(7)	0.032(4)
O6	0.1748(8)	1.2465(19)	0.4188(7)	0.033(4)
O7	0.5034(10)	0.465(2)	0.4174(8)	0.035(4)
O8	0.2222(9)	0.533(2)	0.1842(9)	0.041(5)
O9	0.0783(9)	0.6636(16)	0.2426(7)	0.035(4)
O10	−0.0540(10)	0.9224(17)	0.1285(7)	0.040(4)
O11	0.2181(8)	0.623(2)	0.4743(8)	0.042(5)
O12	0.3571(8)	0.2645(19)	0.4481(6)	0.029(4)
O13	0.0809(9)	0.3131(16)	0.2127(8)	0.036(4)
O14	0.3866(8)	0.7646(19)	0.4817(7)	0.032(4)
O15	−0.1650(9)	1.1537(16)	0.1821(7)	0.033(4)
O16	0.2446(10)	0.9737(17)	0.5130(9)	0.041(5)
O17	0.5228(9)	0.116(2)	0.4527(9)	0.046(5)
O18	0.4726(9)	0.371(2)	0.5333(6)	0.032(4)
O19	0.1899(9)	0.4343(18)	0.3000(7)	0.036(4)
O20	−0.0290(9)	1.000(2)	0.2430(8)	0.033(4)

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

bipyramids (the lone pair occupies an equatorial position), four [PO$_4$] tetrahedra, and two Na$^+$ cations which balance the framework charge. The bond lengths (Table 2) and angles in the [SbO$_4$] and [SbO$_5$] units are comparable to those in antimony (III) phosphates (9, 10) and fluoride phosphates (20); the formation of [SbO$_5$] units occurs only when three-coordinated O atoms, of which there are four, are involved (Fig. 1). The P–O distances (Table 2) and angles, too, are consistent with previously reported antimony phosphates (7–10).

The structure (Fig. 2) can be described in terms of the stacking of two types of layers, **a** and **b**, in the [001] direction. The **a** layer (Fig. 3, top), whose Sb and P atoms lie almost within the same **ab** plane, is constructed from nearly rectangular six-rings, each made up from three [SbO$_4$] and three [PO$_4$] units. The **b** layer (Fig. 3, bottom) is defined by a plane of P atoms. Two sheets of Sb atoms undulate sinusoidally on opposite sides of this plane and the pair of

Sb atoms lying on either side of this plane are connected through oxygen atoms to each other and to the nearest P atom, giving rise to three-rings lying in the *bc* plane. The **b** layer also has four- and six-rings; the six-rings are, like those of the *a* layer, nearly rectangular, but contain three [SbO$_5$], one [SbO$_4$], and two [PO$_4$] units. These layers are connected to each other through three-rings, giving rise to two irregularly shaped eight-rings (Fig. 2). The eight-rings, which contain three [SbO$_5$], two [SbO$_4$], and three [PO$_4$] units, define channels that run in the [010] direction.

The material shows no significant adsorption of N$_2$ at 77 K, displaying a type II isotherm (associated with a non-porous material) (21). This is not surprising since the lone pairs dominate the middle and one side of each channel, while Na$^+$ cations occupy the other side. The Na-O distances (Table 2) for the four nearest O atoms average 2.396 Å as

TABLE 2
Selected Bond Distances

Sb1–O2^i	1.944(16)	P1–O11	1.521(14)
Sb1–O8	2.000(13)	P1–O3	1.541(16)
Sb1–O15^{ii}	2.181(11)	P1–O14	1.558(11)
Sb1–O4^i	2.291(11)	P1–O16	1.559(17)
Sb2–O6^{iii}	1.981(14)	P2–O10	1.512(15)
Sb2–O12	2.121(12)	P2–O15	1.517(13)
Sb2–O16^{iii}	2.149(12)	P2–O4	1.525(13)
Sb2–O11	2.298(12)	P2–O20	1.550(14)
Sb2–O1^{iv}	2.310(11)		
		P3–O9	1.495(13)
Sb3–O2	1.945(12)	P3–O13	1.496(13)
Sb3–O1^v	1.975(13)	P3–O19	1.552(14)
Sb3–O18^v	2.117(13)	P3–O8	1.580(17)
Sb3–O10	2.280(12)		
Sb3–O14^v	2.709(13)	P4–O17	1.509(14)
		P4–O12	1.536(12)
Sb4–O1	2.039(13)	P4–O7	1.542(15)
Sb4–O14	2.112(13)	P4–O18	1.548(14)
Sb4–O7	2.149(14)		
Sb4–O17^{vi}	2.298(14)	Na1–O7^{iv}	2.326(17)
Sb4–O6^{ii}	2.301(12)	Na1–O19	2.392(15)
		Na1–O3	2.428(15)
Sb5–O5	1.976(12)	Na1–O5	2.436(16)
Sb5–O6	2.034(14)	Na1–O17^{iv}	2.650(19)
Sb5–O3	2.203(13)	Na1–O11	2.653(17)
Sb5–O19^{vi}	2.253(13)	Na1–O9	2.663(18)
Sb5–O12^{vi}	2.671(13)		
		Na2–O16^v	2.352(18)
Sb6–O5	1.971(15)	Na2–O16^{ii}	2.394(16)
Sb6–O20	2.010(12)	Na2–O18^x	2.413(15)
Sb6–O13^{vi}	2.186(11)	Na2–O2^i	2.428(15)
Sb6–O9	2.301(11)	Na2–O15^{ii}	2.591(18)
		Na2–O11^v	2.668(18)
		Na2–O17^x	2.685(18)

Note. Symmetry transformations used to generate equivalent atoms: (i) $x + 1/2$, $-y + 1$, z; (ii) $x + 1/2$, $-y + 2$, z; (iii) x, $y − 1$, z; (iv) $x − 1/2$, $-y + 1$, z; (v) $-x + 1/2$, y, $z − 1/2$; (vi) x, $y + 1$, z; (vii) $-x + 1/2$, y, $z + 1/2$; (viii) $x − 1/2$, $-y + 2$, z; (ix) $-x + 1$, $-y + 1$, $z + 1/2$; (x) $-x + 1$, $-y + 1$, $z − 1/2$.
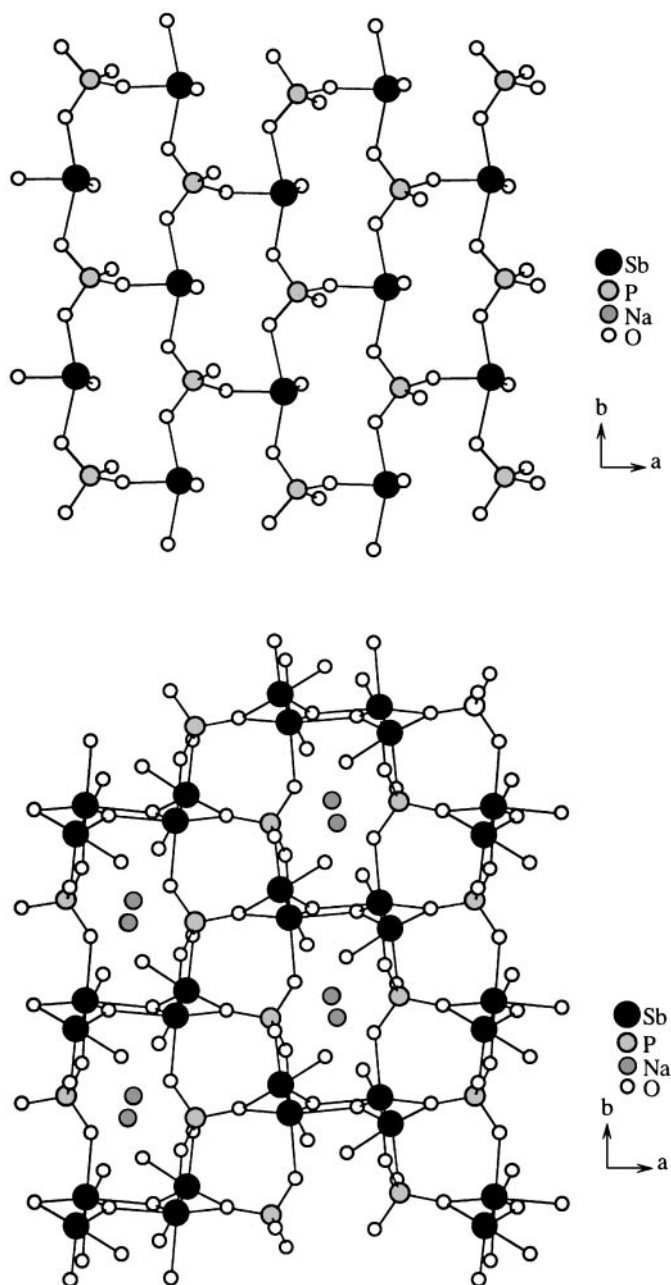
REFERENCES

1. J. M. Thomas, *Angew. Chem. Int. Ed. Engl.* **33,** 913 (1994).
2. S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannon, and E. M. Flanigen, *J. Am. Chem. Soc.* **104,** 1146 (1982).
3. A. K. Cheetham, G. Férey, and T. Loiseau, *Angew. Chem. Int. Ed. Engl.* **38,** 3268 (1999) and references therein.
4. (a) S. Natarajan, M. P. Attfield, and A. K. Cheetham, *Angew. Chem. Intl. Ed. Engl.* **36,** 978 (1997); (b) S. Natarajan and A. K. Cheetham, *J. Chem Soc. Chem. Commun.* **1089** (1997); (c) S. Natarajan and A. K. Cheetham, *J. Solid State Chem.* **134,** 207 (1997); (d) S. Ayyappan, X. Bu, A. K. Cheetham, and C. N. R. Rao, *Chem. Mater.* **10,** 3308 (1998); (e) S. Natarajan, S. Ayyappan, A. K. Cheetham, and C. N. R. Rao, *Chem. Mater.* **10,** 1627 (1998); (f) S. Natarajan, M. Eswaramoorthy, A. K. Cheetham, and C. N. R. Rao, *Chem. Commun.* 1561 (1998).
5. (a) J. B. Parise, *Science* **251,** 293 (1991); (b) X. Wang and F. Liebau, *J. Solid State Chem.* **111,** 385 (1994); (c) X. Wang, *Eur. J. Solid State Inorg. Chem.* **32,** 303 (1995).
6. (a) H. A. Graf and H. Schäfer, *Z. Anorg. Allg. Chem.* **414,** 220 (1975); (b) F. Kluger and F. Pertlik, *Monatsch. Chem.* **116,** 149 (1985); (c) C. Sabelli, I. Nakai, and S. Katsura, *Am. Mineral.* **73,** 398 (1988); (d) U. Simon, F. Schüth, S. Schunk, X. Wang, and F. Liebau, *Angew. Chem. Int. Ed. Engl.* **36,** 1121 (1997).
7. (a) Y. Piffard, A. Lachgar, and M. Tournoux, *Mater. Res. Bull.* **21,** 1231 (1986); (b) Y. Piffard, S. Oyetola, A. Verbaere, and M. Tournoux, *J. Solid State Chem.* **63,** 81 (1986); (c) D. Guyomard, C. Pagnoux, J. J. Zah Letho, A. Verbaere, and Y. Piffard, *J. Solid State Chem.* **90,** 367 (1991); (d) C. Pagnoux, A. Verbaere, Y. Piffard, and M. Tournoux, *Eur. J. Solid State Inorg. Chem.* **30,** 111 (1993); (e) Y. An, S. Feng, Y. Xu, R. Xu, and Y. Yue, *J. Mater. Chem.* **4,** 985 (1994); (f) Y. An, S. Feng, Y. Xu, and R. Xu, *Chem. Mater.* **8,** 356 (1996).
8. (a) A. Verbaere, S. Oyetola, D. Guyomard, and Y. Piffard, *J. Solid State Chem.* **75,** 217 (1988); (b) A. Jouanneaux, A. Verbaere, D. Guyomard, and Y. Piffard, *Eur. J. Solid State Inorg. Chem.* **30,** 125 (1993); (c) K. Kasahara, H. Imoto, and T. Saito, *J. Solid State Chem.* **118,** 104 (1995).
9. B. Kinberger, *Acta Chem. Scand.* **24,** 320 (1970).
10. C. Särnstrand, *Acta Chem. Scand. A* **28,** 275 (1974).
11. B. A. Adair and A. K. Cheetham, unreported results.
12. G. M. Sheldrick, "SADABS User Guide." University of Göttingen, Göttingen, 1995.
13. G. M. Sheldrick, "SHELXL-97, A Program for Crystal Structure Determination." University of Göttingen, Göttingen, 1997.
14. $R(F) = \sum ||F_o| - |F_c||/\sum |F_o|$ against those reflections, where $F^2 > 4\sigma(F^2)$. $R_w(F^2) = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$ against all reflections.
15. R. E. Marsh, V. Schomaker, and F. H. Herbstein, *Acta Crystallogr. Sect. B* **54,** 921 (1998).
16. L. Pauling, "The Nature of the Chemical Bond," 2nd ed. Cornell University Press, Ithaca, NY, 1948.
17. N. W. Alcock, *Adv. Inorg. Chem. Radiochem.* **15,** 1 (1972).
18. D. Zhang, J. Trotter, and F. Aubke, *Inorg. Chem.* **34,** 3153 (1995).
19. (a) I. D. Brown, *J. Solid State Chem.* **11,** 214 (1974), and references therein; (b) J. F. Sawyer and R. J. Gillespie, *Prog. Inorg. Chem.* **34,** 65 (1986), and references therein.
20. (a) K. Holz, F. Obst, and R. Matter, *J. Solid State Chem.* **90,** 353 (1991); (b) S. Hürter, R. Mattes, and D. Rühl, *J. Solid State Chem.* **46,** 204 (1983); (c) K. Holz and R. Mattes, *Z. Anorg. Allg. Chem.* **578,** 133 (1989).
21. K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol, and T. Siemieniewska, *Pure Appl. Chem.* **57,** 603 (1985).
22. (a) M. Catti and G. Ferraris, *Acta Crystallogr. Sect. B* **30,** 1 (1974); (b) M. Baldus, B. H. Meier, R. R. Ernst, A. P. M. Kentgens, H. Meyer zu Altenschildesche, and R. Nesper, *J. Am. Chem. Soc.* **117,** 5141 (1995).
23. B. A. Adair, G. Diaz de Delgado, J. M. Delgado, and A. K. Cheetham, *Angew. Chem. Int. Ed. Engl.,* in press.

FIG. 3. (top) The *a* layer, as defined in Fig. 2, built from Sb_3P_3 rings. (bottom) The *b* layer, built from Sb_4P_2, Sb_2P_2, and Sb_2P rings.

expected (22). While the material does not exhibit porosity, its architecture suggests that Sb^{III} might be incorporated into an open framework. We shall explore this theme in future publications (23).