

Table 2. *Interatomic distances (Å) and their e.s.d.'s*

Bi(1)—S(5)	3.285 (5) 2×	In(3)—S(8)	2.632 (4) 2×
S(7)	3.379 (6) 2×	S(11)	2.702 (5) 2×
S(12)	2.622 (4) 2×	S(4)	2.557 (6)
S(3)	2.883 (6)	S(11)	2.512 (6)
S(9)	2.840 (6)	In(4)—S(2)	2.619 (4) 2×
Bi(2)—S(9)	2.619 (4) 2×	S(10)	2.658 (4) 2×
S(10)	3.232 (5) 2×	S(6)	2.664 (6)
S(11)	3.329 (5) 2×	S(8)	2.584 (6)
S(4)	3.253 (6)	In(5)—S(3)	2.748 (5) 2×
S(5)	2.700 (7)	S(4)	2.552 (4) 2×
Bi(3)—S(1)	2.745 (5) 2×	S(8)	2.635 (6)
S(2)	3.397 (5) 2×	S(12)	2.599 (6)
S(3)	2.912 (5) 2×	In(6)—S(5)	2.604 (4) 2×
S(7)	2.621 (6)	S(6)	2.833 (5) 2×
In(1)—S(1)	2.590 (6) 2×	S(1)	2.657 (7)
S(7)	2.654 (5) 4×	S(10)	2.508 (6)
In(2)—S(2)	2.533 (6) 2×		
S(6)	2.695 (4) 4×		

thermal parameters resulted in a final $R = 0.067^*$ and an average shift/error of 1.5×10^{-5} . Scattering factors of neutral atoms (Cromer & Mann, 1968) were used and corrected for anomalous dispersion. The atomic coordinates are listed in Table 1, bond lengths in Table 2.

Discussion. A view of the complete structure is displayed in Fig. 1. All atoms are located on the mirror planes at $y = 0$ and $\frac{1}{2}$. In(1,2) occupy special positions at the centres of inversion at 000 and $00\frac{1}{2}$, all others being in general positions. In(1–6) are surrounded by six S (distorted octahedra), whereas Bi(1,2) are eightfold (distorted bicapped trigonal prisms), and

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35249 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Antimony(III) Arsenic(V) Oxide

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Abstract. AsSbO_4 , $M_r = 260.67$, monoclinic, $P2_1/m$, $a = 4.794$ (2), $b = 6.925$ (2), $c = 5.307$ (2) Å, $\beta = 93.55$ (2)°, $U = 175.9$ Å³, $Z = 2$, $D_x = 4.923$ Mg m⁻³, $\mu = 17.1$ mm⁻¹ (Mo K α). $R = 5.6\%$ for 500 unique

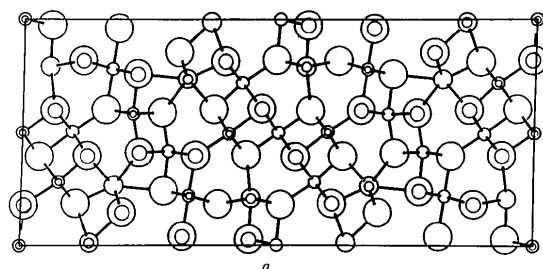


Fig. 1. Structure of $\text{Bi}_3\text{In}_5\text{S}_{12}$ viewed along b ; rings are at $y = \frac{1}{2}$, double rings at $y = 0$ (small: In, medium: Bi, large: S).

Bi(3) is sevenfold (distorted monocapped trigonal prism) coordinated. The In–S distances range from 2.51 to 2.83 Å, the Bi–S from 2.62 to 3.40 Å. The In–S octahedra are edge-shared, and the Bi–S prisms are stacked along y , all forming chains parallel to b . There is only a faint resemblance to $\text{Bi}_2\text{In}_4\text{S}_9$ (Chapuis, Gnehm & Krämer, 1972) where partially sixfold coordinated Bi and fivefold coordinated In were found which do not show up in the structure presented here.

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coordinated by four O in a markedly one-sided manner. All O atoms bridge As and Sb. The compound may be formulated as $\text{As}^{\text{V}}\text{Sb}^{\text{III}}\text{O}_4$.

Introduction. A 1:1 (molar) mixture of Sb_2O_3 (orthorhombic, p.a. Merck) and $\text{As}_2\text{O}_5 \cdot \frac{5}{3}\text{H}_2\text{O}$ (p.a. Merck) was heated to 673 K for 1 week in a gold vessel, itself enclosed in a sealed glass tube. The reaction product was then dried *in vacuo*. It consisted of a white homogeneous polycrystalline mass, out of which numerous extremely thin, colourless, rectangular plates had exuded. Elemental analysis was consistent with the composition AsSbO_4 . The substance is air-stable. The same product resulted with cubic Sb_4O_6 replacing orthorhombic Sb_2O_3 , or with an analogous mixture with reversed oxidation states, *viz* As_4O_6 (cubic, p.a. Merck) and $\text{Sb}_2\text{O}_5 \cdot x\text{H}_2\text{O}$.

A crystal $0.5 \times 0.2 \times 0.001$ mm was used to collect data on a Stoe four-circle diffractometer with monochromated Mo $K\alpha$ radiation. 2033 reflexions forming a full sphere with $7 < 2\theta < 60^\circ$ were measured; after Lp and empirical thin-plate absorption corrections, averaging equivalent reflexions gave 550 unique reflexions, 500 with $F > 4\sigma(F)$.

As and Sb atoms were located by direct methods and O atoms by difference syntheses. Refinement proceeded to $R' = \sum w^{1/2} \Delta / \sum w^{1/2} |F_o| = 0.058$, $R = 0.056$ [As, Sb anisotropic, O isotropic; $w^{-1} = \sigma^2(F) +$

Table 1. Atom coordinates ($\times 10^4$) and isotropic temperature factors ($\text{\AA}^2 \times 10^3$)

	x	y	z	U
Sb	2067 (2)	2500	6782 (2)	15 (1)*
As	7172 (2)	2500	1101 (2)	8 (1)*
O(1)	8348 (25)	2500	8190 (24)	27 (3)
O(2)	3699 (29)	2500	375 (29)	35 (3)
O(3)	8069 (20)	625 (17)	2847 (20)	42 (2)

* Equivalent isotropic U calculated from anisotropic U .

Table 2. Bond lengths (\AA) and angles ($^\circ$)

As—O(2)	1.686 (15)	As—O(3)	1.637 (12)
As—O(1 ^b)	1.677 (14)	O(1 ^v)—Sb	1.975 (13)
O(2 ^{iv})—Sb	2.016 (16)	O(3 ⁱⁱⁱ)—Sb	2.174 (13)
O(1 ^v)—Sb—O(2 ^{iv})	87.1 (7)	O(1 ^v)—Sb—O(3 ⁱⁱⁱ)	86.2 (4)
O(2 ^{iv})—Sb—O(3 ⁱⁱⁱ)	85.8 (4)	O(3 ⁱⁱⁱ)—Sb—O(3 ^{vi})	168.9 (7)
O(2)—As—O(3)	110.5 (5)	O(2)—As—O(1 ^b)	100.0 (8)
O(3)—As—O(1 ^b)	115.5 (5)	O(3)—As—O(3 ^{vi})	104.9 (9)
Sb ^l —O(1)—As ^{iv}	135.3 (8)	As—O(2)—Sb ^{ll}	122.4 (9)
As—O(3)—Sb ⁱⁱⁱ	146.3 (7)		

Symmetry operators

(i)	$1 + x, y, z$	(v)	$-1 + x, y, z$
(ii)	$x, y, -1 + z$	(vi)	$1 - x, 0.5 + y, 1 - z$
(iii)	$1 - x, -y, 1 - z$	(vii)	$x, 0.5 - y, z$
(iv)	$x, y, 1 + z$		

$0.001F^2$]. Final anisotropic thermal parameters U_{11} , U_{22} , U_{33} , U_{13} ($\text{\AA}^2 \times 10^3$) were 14, 20, 11, 2; 13, 1, 10, -2 for Sb and As respectively [all e.s.d.'s 1; temperature-factor exponent defined as $-2\pi^2 (U_{11}h^2a^{*2} + \dots + U_{12}hka^*b^*)$]. The unrealistic U_{22} for As is probably a consequence of the wide and irregular reflexion profiles of a somewhat deformable crystal, which prejudice accurate absorption corrections.

Final atomic coordinates are given in Table 1, bond lengths and angles in Table 2.†

Discussion. As, Sb, O(1) and O(2) lie on special positions $x, \frac{1}{4}, z$ with m symmetry; O(3) lies on a general position. The As atom is coordinated tetrahedrally by O; the average As—O length is 1.66 \AA , compared with 1.68 \AA for the tetrahedral site in both orthorhombic and tetragonal As_2O_5 (Jansen, 1977, 1978, 1979) and 1.69 \AA for the tetrahedral As^{V} site in As_2O_4 (Jones, Beesk, Sheldrick & Schwarzmann, 1980). The ox-

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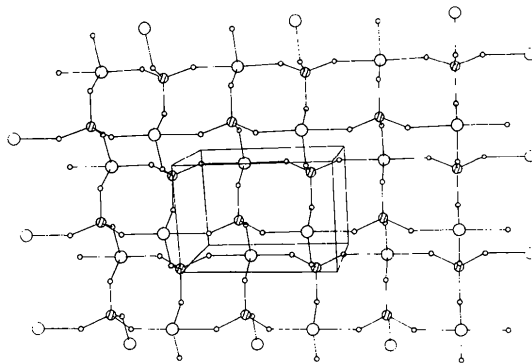


Fig. 1. Perspective view of one layer in AsSbO_4 . Large open circles, Sb^{III} ; hatched circles, As^{V} ; small open circles, O. Axis directions: x vertical, y horizontal, z perpendicular to the paper.

Table 3. Mixed-valence Group Vb oxides

Compound	M^{III} coordination	M^{V} coordination	Reference
$\text{As}^{\text{III}}\text{As}^{\text{V}}\text{O}_4$	3-coordination; at right-angles	tetrahedral	(a)
$\text{Sb}^{\text{III}}\text{As}^{\text{V}}\text{O}_4$	4 coordination; one-sided	tetrahedral	(b)
$\alpha\text{-Sb}^{\text{III}}\text{Sb}^{\text{V}}\text{O}_4$	4 coordination; one-sided	octahedral	(c)
$\beta\text{-Sb}^{\text{III}}\text{Sb}^{\text{V}}\text{O}_4$	4 coordination; one-sided	octahedral	(d)
$\text{Bi}^{\text{III}}\text{Sb}^{\text{V}}\text{O}_4$	4 coordination; one-sided	octahedral	(e)

References: (a) Jones *et al.* (1980); (b) this work; (c) Skapski & Rogers (1965); (d) Rogers & Skapski (1964); (e) Aurivillius (1952).

dation state of As may therefore be taken as +5, *i.e.* the description of the structure with a single net positive charge on As and a single negative charge on Sb should be given most weight. The Sb atom is coordinated by four O atoms in a markedly one-sided manner, similar to the Sb^{III} site in β -Sb₂O₄ (Rogers & Skapski, 1964). This is consistent with the stereochemical influence of an electron lone-pair, *i.e.* with the above description. All O atoms bridge As and Sb.

The extended structure consists of layers parallel to the *xy* plane (Fig. 1); there is one such layer per unit *z* translation. Short Sb...O contacts are 3.06 Å to O(1) at *x, y, z*; 3.04 Å to O(3) at $-1 + x, y, z$; and 3.04 Å to O(3) at $-1 + x, \frac{1}{2} - y, z$ (*e.s.d.*'s 0.02 Å). The latter two (symmetry-related) contacts are between neighbouring layers.

The structure is not closely related to any other mixed-valence Group Vb oxide (Table 3).

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Ammonium Tetrafluorooxovanadate(IV)

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Abstract. (NH₄)₂[VF₄O], orthorhombic, *Pna*2₁, *a* = 7.596 (1), *b* = 12.043 (2), *c* = 5.770 (1) Å, *Z* = 4, *D_m* = 2.25, *D_c* = 2.248 Mg m⁻³, *V* = 527.832 Å³, *M_o K α* (μ = 1.9934 mm⁻¹). The V atom is octahedrally coordinated by five F atoms at V–F distances of 1.910–2.224 Å and one O atom at 1.612 Å. The octahedra are connected through *cis* F atoms to give infinite chains parallel to the *c* axis. There are weak hydrogen bonds between the ammonium ions and the anionic chains with a shortest N...F distance of 2.825 Å. The final *R_i* value is 0.050.

Introduction. There are three ammonium fluorooxovanadates(IV) described in the literature: (NH₄)₃[VF₅O], (NH₄)₂[VF₄O] and (NH₄)₂[VF₄O]·H₂O (Davidovič, Harlamova & Samarec, 1977). They have been characterized by X-ray powder spectra; however, no complete crystal structure determination has been reported.

Crystals of the title compound were prepared in 5% HF solution with a VF₂O:NH₄F molar ratio of 1:3. The space group and preliminary cell dimensions were deduced from oscillation and Weissenberg photographs. Data were collected with an Enraf–Nonius CAD-4 automatic diffractometer in the ω –2 θ mode using Mo *K α* radiation and a graphite mono-

chromator. Accurate cell constants were determined from least-squares analysis of the positions of 30 high-angle reflections. 2082 reflections, measured in the range $1.5 < \theta < 30.0^\circ$, were merged into a unique set of 832 reflections. Of these, 641 were observed with $I_o > 3\sigma(I_o)$ (from counting statistics) and used for the structure analysis. Lorentz–polarization corrections were applied, but no absorption corrections were made.

The position of the V atom was found from a three-dimensional Patterson map. The positions of all non-hydrogen atoms were located from a partially phased Fourier synthesis. All atomic positions, together with individual isotropic temperature factors, were refined by a number of full-matrix least-squares cycles, with all the collected data included, to *R* = 0.067. The structure was then refined with anisotropic temperature factors to *R* = 0.050. H atoms were found in a difference electron-density map. These atoms were included with fixed positional and isotropic thermal parameters ($U_H = 0.07 \text{ \AA}^2$). Atomic scattering factors for H were taken from Stewart, Davidson & Simpson (1965) and for other atoms from Cromer & Mann (1968), those for V, F, O, and N being corrected for the effects of anomalous scattering (Cromer & Liberman, 1970).

The weighting function was determined empirically from: