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Acta Cryst. (1990). **C46**, 2294–2297

Structure of Alkaline-Earth Pentafluoroantimonates(III), $MSbF_5$ ($M = Sr, Ba$)

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(Received 10 April 1990; accepted 16 May 1990)

Abstract. Strontium pentafluoroantimonate(III), $SrSbF_5$, $M_r = 304.36$, orthorhombic, $Pbcm$, $a = 4.378$ (1), $b = 8.853$ (3), $c = 11.233$ (4) Å, $V = 435.4$ (3) Å³, $Z = 4$, $D_m = 4.60$, $D_x = 4.64$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 18.9$ mm⁻¹, $F(000) = 536$, $T = 298$ K, $R = 0.028$ for 596 independent reflections with $I > 3\sigma(I)$. Barium pentafluoroantimonate(III), $BaSbF_5$, $M_r = 354.08$, orthorhombic, $Pbcm$, $a = 4.676$ (1), $b = 9.313$ (2), $c = 11.213$ (3) Å, $V = 488.3$ (2) Å³, $Z = 4$, $D_m = 4.77$, $D_x = 4.82$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 13.6$ mm⁻¹, $F(000) = 608$, $T = 298$ K, $R = 0.015$ for 914 independent reflections with $I > 3\sigma(I)$. $SrSbF_5$ and $BaSbF_5$ are isostructural compounds. The three-dimensional network consists of isolated SbF_5^{2-} units which are connected by ten-coordinated alkaline-earth ions Sr^{2+} or Ba^{2+} . The geometry of these pentafluoroantimonate ions is approximately square pyramidal with the Sb atom outside the pyramid, below the four F atoms constituting the basal plane.

Introduction. Most of the previous works devoted to tin(II), antimony(III) or tellurium(IV) compounds have emphasized the prominent role played by the free electron pair, usually leading to original structures (Gillespie & Nyholm, 1957; Fourcade & Masherpa, 1978).

In particular, the reaction of SbF_3 with monovalent fluorides gives various series of fluorocomplexes: M_2SbF_5 (Byström & Wilhelmi, 1951b; Ryan & Cromer, 1972; Habibi, Ducourant, Fourcade & Masherpa, 1974a), $MSbF_4$ (Byström, Bäcklund & Wilhelmi, 1951; Byström, Bäcklund & Wilhelmi, 1952; Mehrain, Ducourant, Fourcade &

Masherpa, 1974; Habibi, Bonnet & Ducourant, 1978), MSb_2F_7 (Byström & Wilhelmi, 1951a; Ryan, Mastin & Larson, 1971; Mastin & Ryan, 1971; Habibi, Ducourant, Fourcade & Masherpa, 1974b), MSb_4F_{13} (Byström & Wilhelmi, 1950; Ducourant, Fourcade, Philippot & Masherpa, 1975), MSb_3F_{10} (Fourcade, Masherpa & Philippot, 1975; Ducourant, Bonnet, Fourcade & Masherpa, 1975), $M_4Sb_5F_{19}$ and $M_3Sb_4F_{15}$ (Ducourant & Fourcade, 1976). Structural determinations have been carried out on some of them.

SbF_5^{2-} units have so far been found only in the presence of alkali ions (Na^+ , K^+ , Rb^+ , Cs^+) as well as with NH_4^+ and Tl^+ . The possible existence of homologous species in other compounds prompted us to investigate the alkaline-earth fluoride-antimony trifluoride systems. The present paper reports the single-crystal structure determination of $SrSbF_5$ and $BaSbF_5$.

Experimental. The two compounds $SrSbF_5$ and $BaSbF_5$ were prepared by solid-state reactions from stoichiometric mixtures of SbF_3 and MF_2 ($M = Sr, Ba$). The starting materials were mixed in a dry glove box, introduced into gold tubes and heated under vacuum at 393 K. The tubes were then sealed in a dry argon atmosphere and heated over 15 h at 573 K. Single crystals were obtained by heating $SrSbF_5$ and $BaSbF_5$ to 783 and 903 K respectively, then by slow cooling (3 K h^{-1}) to 403 K. D_m values were obtained by hydrostatic methods.

Orthorhombic symmetry was deduced from Laue, Weissenberg and precession photographs. Cell parameters were determined from an X-ray powder

Table 1. Details of data collection and refinement for SrSbF₅ and BaSbF₅

	SrSbF ₅	BaSbF ₅
Crystal colour	Translucent, colourless	Translucent, colourless
Crystal form and size (μm)	Parallelepiped 30 × 40 × 60	Sphere r ≈ 45
(sin θ/λ) _{max} (Å ⁻¹)	0.81	0.81
Transmission factor range	0.481 < T < 0.495	0.418 < T < 0.435
Index range h	-7 → 7	-7 → 7
k	-14 → 14	-14 → 14
l	0 → 11	0 → 17
Monochromator	Graphite	Graphite
Scan type	ω-2θ	ω-2θ
Scan angle (°)	0.90 + 0.35 tan θ	0.80 + 0.35 tan θ
Counter slit width (mm)	2.50 + 4.30 tan θ	2.00 + 4.60 tan θ
ΔI/I (%) for the three control reflections	5.6	4.5
No. of measured reflections	3019	4470
No. of unique reflections with I > 3σ(I)	596	914
R _{int} (%)	1.6	1.7
No. of parameters refined	37	37
Weighting scheme	1/σ ² (F _o)	1/σ ² (F _o)
Extinction parameter in F _o = F(1 - 10 ⁻⁴ × xF ² /sin θ)	92 (2) × 10 ⁻⁴	14.3 (9) × 10 ⁻⁴
R	0.028	0.015
wR	0.035	0.022
S	1.363	0.868
Max. shift/e.s.d.	0.001	0.002
Max. of residual (e Å ⁻³)	1.4 (near Sb)	1.6 (near Ba)

diffraction pattern (graphite-monochromated Cu Kα radiation and Si as internal standard) using 25 reflections (7 < θ < 29°) for SrSbF₅ and 28 reflections (9 < θ < 28°) for BaSbF₅. Conditions of the data collection with an Enraf-Nonius CAD-4 diffractometer are shown in Table 1. Corrections were made for Lorentz-polarization effects but not for absorption.

Systematic absences $k = 2n + 1$ for $0kl$ and $l = 2n + 1$ for $h0l$ consistent with two possible space groups: $Pbcm$ and $Pbc2_1$. Atomic scattering factors for Ba²⁺, Sr²⁺, Sb³⁺ and F⁻ and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Structure determined in space group $Pbcm$ by the heavy-atom method with program *SHELX76* (Sheldrick, 1976) and IBM 3090-400 computer of the Computing Center of Montpellier. Structure of BaSbF₅ was solved first. Sites of Ba²⁺ and Sb³⁺ ions were found by Patterson function deconvolution ($R \approx 0.17$) and F⁻ ions were located with several difference Fourier syntheses.

Structural parameters of SrSbF₅ were obtained based on the hypothesis of isostructurality. Details of final refinements with weighting scheme and empirical isotropic extinction parameter are indicated in Table 1. Reliability factors lowered to $R = 0.028$ and $wR = 0.035$ for SrSbF₅ and to $R = 0.015$ and $wR =$

0.022 for BaSbF₅. Calculations with the non-centrosymmetric group $Pbc2_1$ did not improve the model. The final atomic parameters of the two compounds are given in Table 2 and selected bond lengths and angles are listed in Table 3.*

Discussion. Projections of the structure along [100] and along [001] are presented in Fig. 1. The three-dimensional network may be described in terms of independent SbF₅²⁻ fluoro anions connected to MF₁₀ alkaline-earth polyhedra.

The site of Sb³⁺ consists of a distorted SbF₅E²⁻ octahedron. The cation is located outside the pyramid formed by the five F⁻ ions. The presence of the lone pair yields the typical environment which has already been reported in numerous other ternary antimony fluorides, for example in M₂SbF₅ (M = Na, K, NH₄, Tl) and KSbF₄. The same environment has been found in the two compounds SrSbF₅ and

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53244 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

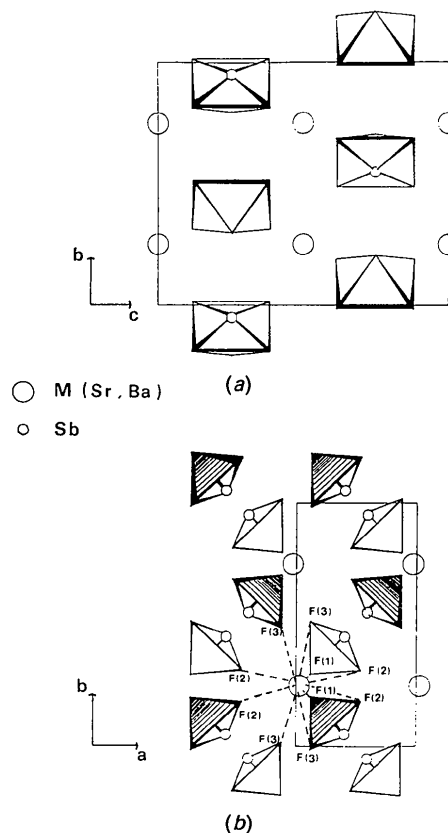


Fig. 1. Projections of the MSbF₅ (M = Sr, Ba) structure: (a) along [100] and (b) along [001].

Table 2. Atomic parameters and equivalent isotropic temperature factors (estimated standard deviations in parentheses)

$$B_{\text{eq}} = \frac{8}{3}\pi^2 \sum_{i=1}^3 \sum_{j=1}^3 a_i^* a_j^* U_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	Position	Site symmetry	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
SrSbF₅						
Sr	4(c)	2..	0.0084 (1)	$\frac{1}{4}$	0	0.826 (17)
Sb	4(d)	..m	0.3890 (1)	0.0537 (1)	$\frac{1}{4}$	0.839 (17)
F(1)	4(d)	..m	0.0758 (10)	0.2124 (5)	$\frac{1}{4}$	1.56 (15)
F(2)	8(e)	1	0.4793 (7)	0.7011 (4)	0.1118 (4)	1.96 (12)
F(3)	8(e)	1	0.0878 (8)	0.9870 (4)	0.1140 (4)	1.81 (12)
BaSbF₅						
Ba	4(c)	2..	0.02762 (5)	$\frac{1}{4}$	0	0.853 (5)
Sb	4(d)	..m	0.40594 (6)	0.04943 (3)	$\frac{1}{4}$	1.016 (5)
F(1)	4(d)	..m	0.1184 (6)	0.2040 (3)	$\frac{1}{4}$	1.48 (5)
F(2)	8(e)	1	0.4573 (4)	0.6873 (3)	0.1148 (2)	2.16 (5)
F(3)	8(e)	1	0.1189 (6)	0.9856 (2)	0.1174 (2)	2.09 (5)

Table 3. Selected bond lengths (Å) and angles (°) in MSbF₅ (M = Sr, Ba) (e.s.d.'s in parentheses)

	M = Sr	M = Ba
Sb—F(1)	1 × 1.963 (4)	1 × 1.970 (3)
Sb—F(2 ⁱ)	2 × 2.108 (4)	2 × 2.087 (2)
Sb—F(3 ⁱⁱ)	2 × 2.103 (4)	2 × 2.090 (2)
F(1)—F(2 ⁱ)	2 × 2.493 (5)	2 × 2.502 (3)
F(1)—F(3 ⁱⁱ)	2 × 2.514 (5)	2 × 2.520 (3)
F(2 ⁱ)—F(2 ⁱⁱⁱ)	1 × 3.106 (8)	1 × 3.032 (4)
F(3 ⁱⁱ)—F(3 ^{iv})	1 × 3.055 (8)	1 × 2.974 (4)
F(2 ⁱ)—F(3 ⁱⁱ)	2 × 2.680 (8)	2 × 2.731 (4)
F(1)—Sb—F(2 ⁱ)	75.4 (1)	76.1 (1)
F(1)—Sb—F(3 ⁱⁱ)	76.3 (1)	76.7 (1)
F(2 ⁱ)—Sb—F(2 ⁱⁱⁱ)	94.8 (2)	93.2 (1)
F(2 ⁱ)—Sb—F(3 ⁱⁱ)	79.1 (1)	81.7 (1)
F(3 ⁱⁱ)—Sb—F(3 ^{iv})	93.2 (2)	90.7 (1)
M—F(1)	2 × 2.843 (1)	2 × 2.867 (1)
M—F(2 ⁱ)	2 × 2.515 (3)	2 × 2.672 (2)
M—F(2 ⁱⁱ)	2 × 2.606 (3)	2 × 2.793 (2)
M—F(3 ⁱⁱ)	2 × 2.494 (4)	2 × 2.649 (2)
M—F(3 ^{iv})	2 × 2.680 (4)	2 × 2.825 (2)
(M—F)	2.628	2.761

Symmetry code: (i) $1-x, y-\frac{1}{2}, z$; (ii) $x, y-1, z$; (iii) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iv) $x, y-1, \frac{1}{2}-z$; (v) $-x, y-\frac{1}{2}, z$; (vi) $-x, 1-y, -z$.

BaSbF₅. The distance separating the Sb atom from the rectangular base of the pyramid is approximately the same: 0.51 Å in SrSbF₅ and 0.50 Å in BaSbF₅.

Fig. 2(a) shows the thermal ellipsoids determined for the so-called equatorial [F(2) and F(3)] and axial F(1) fluorine ions constituting this unit. As expected, the presence of the lone pair *E* in the axial direction induces a distortion of the octahedron around the Sb atom. The *E*—F(2) and *E*—F(3) interactions, which are strongest, lead to an Sb—F(1) bond (1.963 Å for SrSbF₅ and 1.970 Å for BaSbF₅) shorter than Sb—F(2) and Sb—F(3) bonds (greater than 2 Å). For the same reasons F(1)—Sb—F(2) and F(1)—Sb—F(3) angles are always less than 90° (from 75.4 to 76.7°).

In addition it should be noticed that the alkaline-earth ions ensure a strong cohesion between the neighbouring SbF₅E²⁻ units since the F(2)···F(2) and

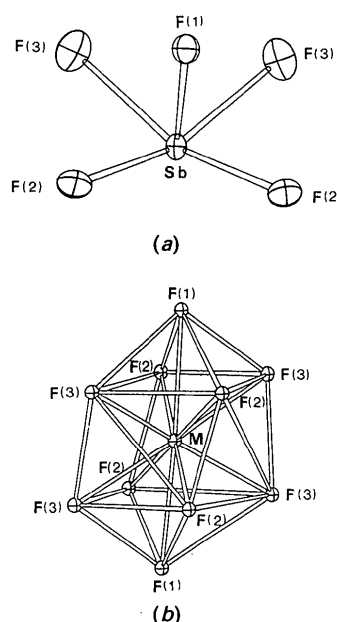


Fig. 2. Structural representations of the cationic environments: (a) for antimony and (b) for the alkaline-earth atom.

F(3)···F(3) interpyramidal distances are shorter than the F(2)···F(2) and F(3)···F(3) intrapyramidal ones. The following values (Å) have been found:

in SrSbF₅

$$\begin{aligned} \text{F(2)} \cdots \text{F(2)}_{\text{interpyr.}} &= 2.656 & \text{F(3)} \cdots \text{F(3)}_{\text{interpyr.}} &= 2.684 \\ \text{F(2)} \cdots \text{F(2)}_{\text{intrapyr.}} &= 3.106 & \text{F(3)} \cdots \text{F(3)}_{\text{intrapyr.}} &= 3.055; \end{aligned}$$

in BaSbF₅

$$\begin{aligned} \text{F(2)} \cdots \text{F(2)}_{\text{interpyr.}} &= 2.827 & \text{F(3)} \cdots \text{F(3)}_{\text{interpyr.}} &= 2.870 \\ \text{F(2)} \cdots \text{F(2)}_{\text{intrapyr.}} &= 3.032 & \text{F(3)} \cdots \text{F(3)}_{\text{intrapyr.}} &= 2.974. \end{aligned}$$

Every alkaline-earth ion is coordinated by ten F⁻ ions which build up a distorted 4.4.1.1. bicapped cube (Fig. 2b). Such an environment is unusual for large M²⁺ cations in fluorides: indeed in most cases

the coordination found for Sr^{2+} or Ba^{2+} is eight, nine or twelve (Von der Mühl & Ravez, 1974; Von der Mühl, Daut & Ravez, 1973; Von der Mühl, Andersson & Galy, 1971; Abjean, Leblanc, De Pape & Ferey, 1985).

As could be expected, the Sr—F distances are shorter than the Ba—F ones, as shown in Table 3. The MF_{10} polyhedron is somewhat distorted, but nevertheless less so than in other fluorinated compounds (De Kozak, Leblanc, Samouël, Ferey & De Pape, 1981). In SrSbF_5 and BaSbF_5 two SbF_5 pyramids share one face [F(1), F(2), F(3)] with this polyhedron, whereas four other pyramids are linked to the polyhedron by one apex.

Every F^- ion exhibits a threefold coordination with the cations (1Sb^{3+} and 2M^{2+}), thus ensuring a strong connection in the three-dimensional network: the F(1) ions are tied to the M^{2+} ion along the z direction, whereas the F(2) and F(3) ions are bonded to this divalent cation along x and y respectively (Fig. 1*b*). Such an environment leads to the following electrostatic valence for fluorine: $e.v. = (1 \times \frac{3}{5}) + (2 \times \frac{2}{10}) = 1$. The identical result obtained for the three types of fluorine ions [F(1), F(2) and F(3)] is in good agreement with the counteraction observed in the interatomic distances: $\text{Sb—F(1)} < \text{Sb—F(2,3)}$ is correlated with $\text{M—F(1)} > \text{M—F(2,3)}$.

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Acta Cryst. (1990). **C46**, 2297–2299

Silver Dicyanamide, $\text{AgN}(\text{CN})_2$ – Orthorhombic Modification

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(Received 2 February 1990; accepted 9 May 1990)

Abstract. $M_r = 173.9$, orthorhombic, $Pnma$, $a = 16.133$ (8), $b = 3.612$ (2), $c = 5.983$ (3) Å, $V/Z = 87.2$ (1) Å³, $Z = 4$, $D_x = 3.313$ (4) g cm⁻³, Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å, $\mu = 456$ cm⁻¹, $F(000) = 320$, $T = 296$ (2) K, $R = 0.086$ for 331 reflections. The structure consists of infinite chains, —Ag—N≡C—N—C≡N—Ag—, running parallel to the a direction. This is similar to the arrangement found in the trigonal form previously reported, except that the 3_1 axis along the chain is replaced

here by a 2_1 axis. The interatomic distances and angles are not significantly different from those found in the trigonal form.

Introduction. The crystal structure of trigonal $\text{AgN}(\text{CN})_2$ was reported previously (Britton & Chow, 1977). At the time that that structure was determined, the first crystal examined was not identical with the trigonal crystals that comprised the bulk of the sample. The crystal was of poor quality and