

Tris(*N,N,N',N'*-tetramethylguanidinium)
nonabromodiantimonate(III)

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In the title compound, $[\text{NH}_2\text{C}(\text{N}(\text{CH}_3)_2)_2]_3[\text{Sb}_2\text{Br}_9]$, the organic cations interact with the isolated $[\text{Sb}_2\text{Br}_9]^{3-}$ anions by way of $\text{N}-\text{H}\cdots\text{Br}$ hydrogen bonds, leading to some deformations of the inorganic unit.

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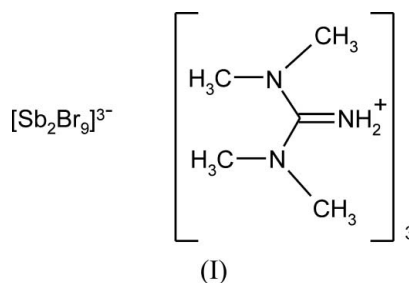
Key indicators

Single-crystal X-ray study
 $T = 295 \text{ K}$
 Mean $\sigma(\text{Sb}-\text{Br}) = 0.001 \text{ \AA}$
 R factor = 0.033
 wR factor = 0.067
 Data-to-parameter ratio = 20.0

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Comment

This study is a continuation of our investigations on the syntheses, structures and phase transitions of halogenoantimonate(III) and halogenobismuthate(III) anions in combination with organic cations (*e.g.* Bujak & Angel, 2005, 2006; Zarychta & Zaleski, 2006).



The asymmetric unit of the title compound, (I), consists of one isolated $[\text{Sb}_2\text{Br}_9]^{3-}$ anion and three crystallographically distinct *N,N,N',N'*-tetramethylguanidinium cations (Fig. 1). The inorganic ions are built up from two distorted $[\text{SbBr}_6]^{3-}$ octahedra sharing one face. This distortion is predicted for an AX_6E geometry (A = central atom, X = ligand, E = unshared electron pair) on the basis of the valence-shell electron-pair repulsion (VSEPR) model (Gillespie & Robinson, 2005).

The geometry of the $[\text{Sb}_2\text{Br}_9]^{3-}$ anion in (I) is similar to that seen for the same anion in other compounds (Hubbard & Jacobson, 1972; Hall *et al.*, 1986), with the terminal $\text{Sb}-\text{Br}$ bonds significantly shorter than the bridging ones (Table 1). The *trans* influence is evident (*e.g.* Landrum & Hoffmann, 1998). The interatomic $\text{Br}-\text{Sb}-\text{Br}$ angles involving the terminal Br atoms are greater than the ideal 90° , whereas those between the bridging ones are less than 90° . The average $\text{Sb}-\text{Br}-\text{Sb}$ angle is $78.28(2)^\circ$ (Table 1).

The organic cations are located between the inorganic anions (Fig. 2). Their geometries are comparable to those previously reported (*e.g.* Bujak *et al.*, 1999). The NH_2^+ groups of the cations face the bromine atoms. The CN_3 guanidine portions of cations are planar, with the $\text{N}-\text{C}$ distances ranging from $1.320(7)$ to $1.332(6) \text{ \AA}$ (partial double-bond character). The *N,N*- and *N',N'*-dimethylammonium groups are twisted with respect to each other, on average, by about 55° .

The organic cations are linked to the $[\text{Sb}_2\text{Br}_9]^{3-}$ anion through relatively weak $\text{N}-\text{H}\cdots\text{Br}$ hydrogen bonds (Table 2

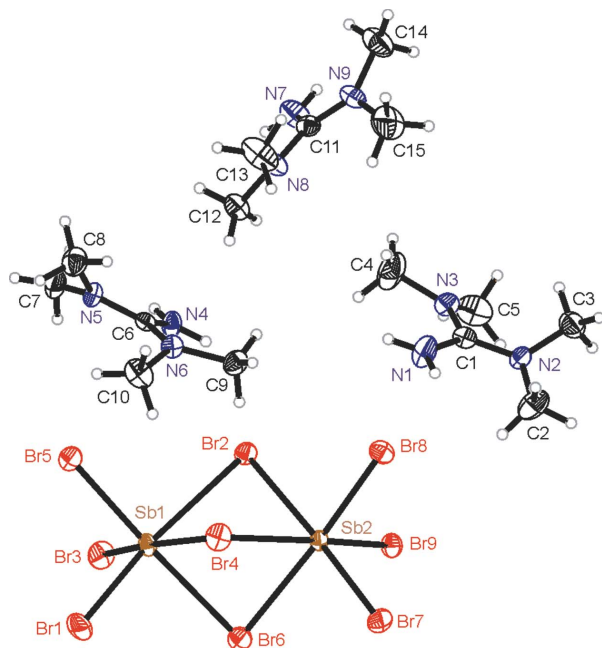


Figure 1
The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are plotted at the 25% probability level.

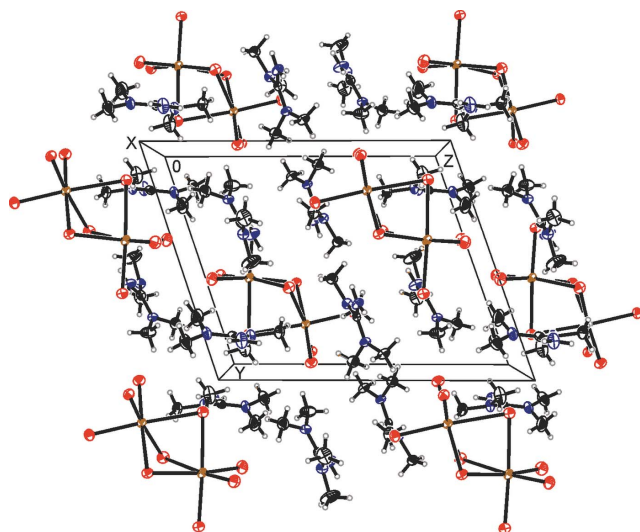


Figure 2
A packing diagram of (I). Displacement ellipsoids are plotted at the 25% probability level.

and Fig. 3) which are partly responsible for the distorted octahedral Sb^{III} coordination, both in terms of differences between equivalent $\text{Sb}-\text{Br}$ bond lengths as well as $\text{Br}-\text{Sb}-\text{Br}$ angles. These influences are visible in the case of the bridging (Br2, Br4 and Br6) atoms. The presence of the hydrogen bonds leads to changes of the $\text{Sb}-\text{Br}$ bridging-bond lengths from the shortest $\text{Sb1}-\text{Br6}$ [3.0038 (8) Å] to the longest $\text{Sb1}-\text{Br2}$ [3.1692 (7) Å], the average being 3.0721 Å. The terminal $\text{Sb}-\text{Br}$ bonds are in the range from the shortest $\text{Sb1}-\text{Br1}$ [2.5672 (7) Å] to the longest $\text{Sb2}-\text{Br9}$ [2.6694 (7) Å] with an average value of 2.6301 Å. The deformation of the Sb1 octahedron, taking into account the differences in $\text{Sb}-\text{Br}$ distances, is larger than that of Sb2 .

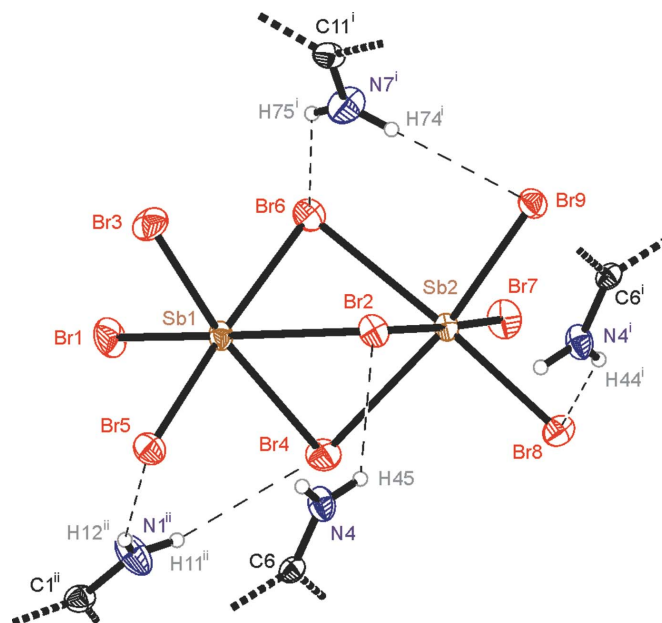


Figure 3
Detail of (I) showing the bioctahedral $[\text{Sb}_2\text{Br}_9]^{3-}$ anion and hydrogen bonds (dashed lines) arising from nearby organic fragments. Displacement ellipsoids are drawn at the 25% probability level. [Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $1-x, 1-y, 1-z$.]

Experimental

Crystals of (I) were obtained at room temperature by crystallization from a solution of concentrated hydrobromic acid containing antimony(III) oxide and N,N,N',N' -tetramethylguanidine. The molar ratio of Sb^{III} to organic cation was varied from 2:1 to 1:10.

Crystal data

$(\text{C}_5\text{H}_{14}\text{N}_3)_3[\text{Sb}_2\text{Br}_9]$
 $M_r = 1311.27$
 Triclinic, $P\bar{1}$
 $a = 10.9824$ (5) Å
 $b = 12.1782$ (7) Å
 $c = 15.0405$ (8) Å
 $\alpha = 71.064$ (5)°
 $\beta = 88.199$ (4)°
 $\gamma = 85.024$ (4)°
 $V = 1895.56$ (17) Å³

$Z = 2$
 $D_x = 2.297$ Mg m⁻³
 $D_m = 2.30$ (2) Mg m⁻³
 D_m measured by flotation in $\text{CCl}_4/\text{CHBr}_3$
 Mo $K\alpha$ radiation
 $\mu = 10.93$ mm⁻¹
 $T = 295$ (2) K
 Pillar, yellow
 $0.25 \times 0.25 \times 0.15$ mm

Data collection

Oxford Diffraction Xcalibur CCD diffractometer
 ω scans
 Absorption correction: multi-scan (*XPRED* in *SHELXTL*; Sheldrick, 1990)
 $T_{\text{min}} = 0.088$, $T_{\text{max}} = 0.194$

11715 measured reflections
 6607 independent reflections
 4616 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.037$
 $\theta_{\text{max}} = 25.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.067$
 $S = 0.90$
 6607 reflections
 330 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0249P)^2]$
 $(\Delta\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.62$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.71$ e Å⁻³

Table 1

Selected bond lengths (Å).

Sb1—Br1	2.5672 (7)	Sb2—Br2	3.0124 (7)
Sb1—Br2	3.1692 (7)	Sb2—Br4	3.0671 (7)
Sb1—Br3	2.5936 (7)	Sb2—Br6	3.0629 (8)
Sb1—Br4	3.1174 (7)	Sb2—Br7	2.6319 (7)
Sb1—Br5	2.6644 (8)	Sb2—Br8	2.6542 (7)
Sb1—Br6	3.0038 (8)	Sb2—Br9	2.6694 (7)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1—H12···Br5 ⁱ	0.86	2.70	3.495 (5)	154
N1—H11···Br4 ⁱ	0.86	2.85	3.588 (5)	145
N4—H44···Br8 ⁱⁱ	0.86	2.90	3.635 (4)	144
N4—H45···Br2	0.86	2.89	3.552 (5)	135
N7—H75···Br6 ⁱⁱ	0.86	2.77	3.416 (5)	133
N7—H74···Br9 ⁱⁱ	0.86	2.90	3.711 (6)	158

 Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x, -y + 1, -z + 1$.

The H atoms were positioned geometrically (C—H = 0.96 Å and N—H = 0.86 Å) and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ or $1.5U_{\text{eq}}(\text{C})$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2001); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2004); data reduc-

tion: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

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