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Triammonium nonaiododiantimonate(III), $(NH_4)_3[Sb_2I_9]$

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The crystal structure of the title compound, $(NH_4)_3[Sb_2I_9]$, which crystallizes in the monoclinic space group $P2_1/n$, resembles that of hexagonal $Cs_3[Sb_2I_9]$, which crystallizes in space group $P\overline{3}m1$. The title compound consists of double layers parallel to (001). Each layer is made up of distorted corner-sharing SbI_6 octahedra. One-third of the ammonium cations reside within six-membered rings formed by corner-sharing SbI_6 octahedra within the layers. The other ammonium cations are situated within three-membered rings built from corner-sharing SbI_6 octahedra near the edges of the layers.

Key indicators

Single-crystal X-ray study
T = 223 K
Mean σ(I–Sb) = 0.001 Å
H-atom completeness 0%
R factor = 0.041
wR factor = 0.089
Data-to-parameter ratio = 46.8

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

Comment

While attempting to prepare antimony cyanamide from cyanamide and Sb_2O_3 in an HI solution to dissolve the latter, cyanamide decomposed into ammonia and we obtained crystals of $(NH_4)_3[Sb_2I_9]$ instead.

The structure of the title compound is shown in Fig. 1 in a view approximately along the b axis. It consists of double layers parallel to (001). Each layer is built up of SbI_6 octahedra by corner-sharing. There are two crystallographically independent Sb atoms, each octahedrally coordinated by six I atoms (Fig. 2). The SbI_6 octahedra are considerably distorted, displaying Sb–I bond lengths from 2.8422 (9) to 3.2211 (9) Å. The Sb(1)I_6 octahedron corner-shares with two Sb(1)I_6 octahedra and one Sb(2)I_6 octahedron, and the Sb(2)I_6 octahedron corner-shares with two Sb(2)I_6 octahedra and one Sb(1)I_6 octahedron. This arrangement leads to the formation of six-membered rings (Fig. 3) within the layers, in which one-third of the ammonium cations (N1) reside. N2 and N3 are

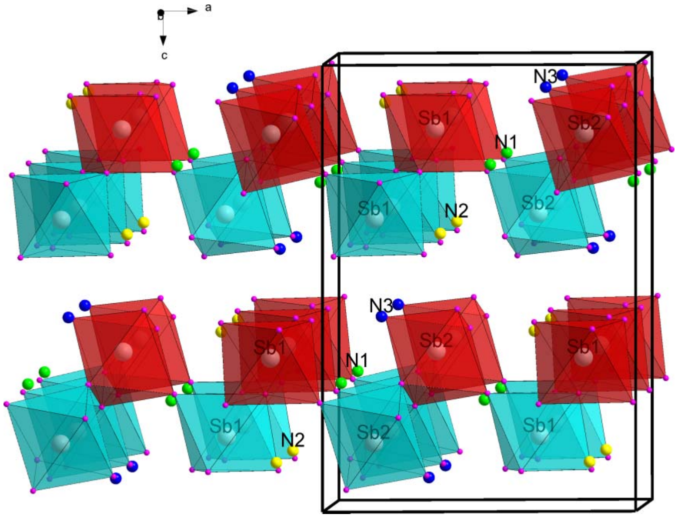

Figure 1
The structure of $(NH_4)_3[Sb_2I_9]$, viewed approximately along [010].

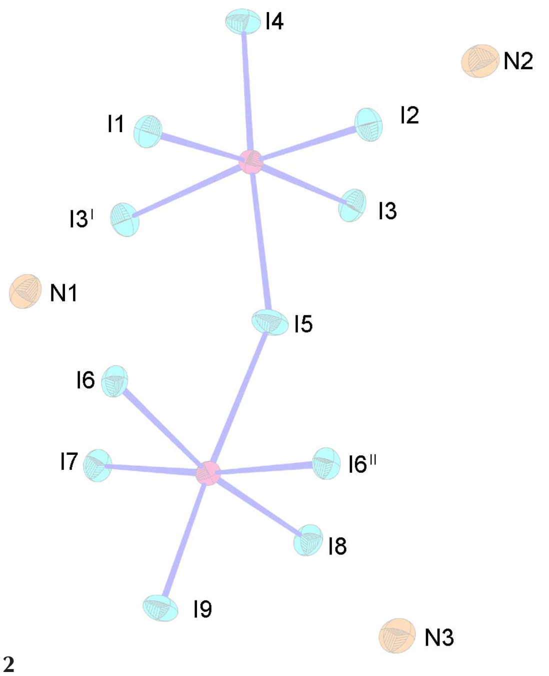

Figure 2
Two corner-sharing SbI_6 octahedra with surrounding N atoms. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x - \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$.

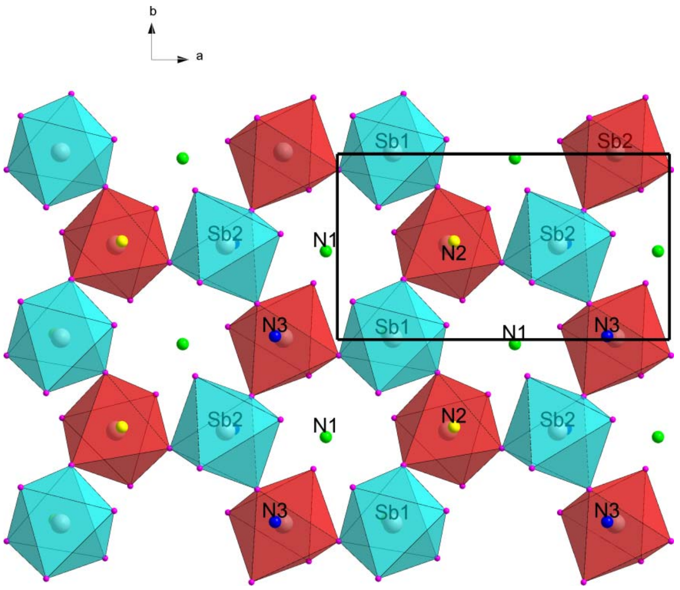

Figure 3
Projection of the structure along [001], showing the six-membered rings built of SbI_6 octahedra.

situated inside three-membered rings built of corner-sharing SbI_6 octahedra near the edges of the layers. The ammonium cations are stabilized by hydrogen bonding to the surrounding I atoms.

The structure of $(NH_4)_3[Sb_2I_9]$ resembles that of one modification of its caesium analogue, $Cs_3[Sb_2I_9]$, which crystallizes in space group $P\bar{3}m1$ (Arakcheeva *et al.*, 1999). In the trigonal structure, similar but more regular double layers with identical-membered rings were observed; in the higher symmetry structure, the Cs cations are surrounded by twelve I atoms. The second modification of $Cs_3[Sb_2I_9]$ was described by Chabot & Parthé (1978) and crystallizes in the hexagonal $Cs_3Cr_2Cl_9$ structure type in space group $P6_3/mmc$, but it shows no topological relation to the title compound.

Experimental

$(NH_4)_3[Sb_2I_9]$ was obtained by reaction of Sb_2O_3 (10 mmol) and H_2NCN (cyanamide, 30 mmol) in an HI solution (2 *M*, 60 ml). Prismatic red crystals were grown by slow evaporation at room temperature after several days.

Crystal data

$(NH_4)_3[Sb_2I_9]$
$M_r = 1439.75$
Monoclinic, $P2_1/n$
$a = 14.394$ (3) Å
$b = 8.0685$ (18) Å
$c = 20.505$ (5) Å
$\beta = 90.530$ (4)°
$V = 2381.4$ (9) Å^3
$Z = 4$

$D_x = 4.016$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 5949 reflections
$\theta = 1.7$–28.4°
$\mu = 13.92$ mm^{-1}
$T = 223$ (2) K
Prism, red
0.15 × 0.12 × 0.10 mm

Data collection

Bruker SMART APEX CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
$T_{\min} = 0.151$, $T_{\max} = 0.251$
31497 measured reflections

5949 independent reflections
4013 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.067$
$\theta_{\max} = 28.4°$
$h = -19 \rightarrow 19$
$k = -10 \rightarrow 10$
$l = -27 \rightarrow 27$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.089$
$S = 1.01$
5949 reflections
127 parameters
H atoms not located

$w = 1/[\sigma^2(F_o^2) + (0.0263P)^2 + 6.8306P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.09$ e Å^{-3}
$\Delta\rho_{\min} = -0.98$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Sb1—I1	2.8556 (8)	Sb2—I8	2.8422 (9)
Sb1—I4	2.8591 (9)	Sb2—I7	2.8602 (9)
Sb1—I2	2.8725 (9)	Sb2—I9	2.8664 (9)
Sb1—I5	3.1579 (10)	Sb2—I5	3.1501 (10)
Sb1—I3^{iii}	3.1633 (9)	Sb2—I6^{ii}	3.1865 (9)
Sb1—I3	3.1956 (9)	Sb2—I6	3.2211 (9)
I1—Sb1—I4	94.08 (3)	I7—Sb2—I9	94.32 (3)
I1—Sb1—I2	92.26 (3)	I8—Sb2—I5	89.32 (3)
I4—Sb1—I2	93.42 (3)	I7—Sb2—I5	92.12 (2)
I1—Sb1—I5	92.65 (3)	I9—Sb2—I5	173.14 (3)
I4—Sb1—I5	173.12 (3)	I8—Sb2—I6^{ii}	90.78 (3)
I2—Sb1—I5	87.74 (2)	I7—Sb2—I6^{ii}	173.49 (3)
I1—Sb1—I3^{iii}	88.60 (3)	I9—Sb2—I6^{ii}	89.90 (2)
I4—Sb1—I3^{iii}	92.29 (2)	I5—Sb2—I6^{ii}	83.48 (2)
I2—Sb1—I3^{iii}	174.15 (3)	I8—Sb2—I6	171.27 (3)
I5—Sb1—I3^{iii}	86.44 (2)	I7—Sb2—I6	91.94 (2)
I1—Sb1—I3	173.51 (3)	I9—Sb2—I6	93.36 (3)
I4—Sb1—I3	87.33 (3)	I5—Sb2—I6	84.04 (3)
I2—Sb1—I3	93.98 (3)	I6^{ii}—Sb2—I6	82.85 (2)
I5—Sb1—I3	85.83 (3)	Sb1^i—I3—Sb1	146.98 (2)
I3^{iii}—Sb1—I3	85.02 (2)	Sb2—I5—Sb1	151.96 (3)
I8—Sb2—I7	93.98 (3)	Sb2^{iv}—I6—Sb2	149.68 (2)
I8—Sb2—I9	92.59 (3)		

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

The H positions of the ammonium cations could not be determined. The maximum residual electron density is 1.07 Å from I6, and the minimum electron density is 1.56 Å from Sb1.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 2002) and *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXL97*).

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