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Key indicators

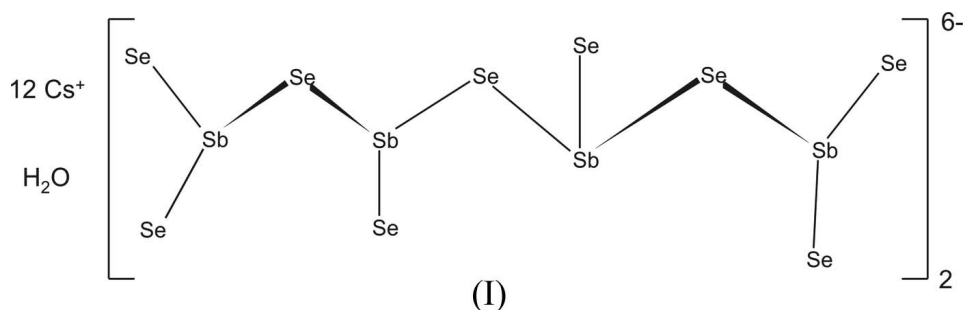
Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{b-Se}) = 0.003\text{ \AA}$
H-atom completeness 0%
Disorder in main residue
 R factor = 0.067
 wR factor = 0.135
Data-to-parameter ratio = 28.8For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Hexacaesium nonaselenidotetraantimonate(III)
hemihydrate

The title compound, $\text{Cs}_6\text{Sb}_4\text{Se}_9 \cdot 0.5\text{H}_2\text{O}$, contains discrete $[\text{Sb}_4\text{Se}_9]^{6-}$ chain anions consisting of corner-linked SbSe_3 pyramids. Molecular C_2 symmetry is observed for these nonaselenidoantimonate(III) anions, which exhibit bridging Sb-Se distances in the range 2.615 (2)–2.650 (3) Å and shorter terminal Sb-Se distances between 2.507 (3) and 2.522 (3) Å.

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Comment

Although electrospray mass spectrometric measurements on the $\text{K}^+/\text{Sb}/\text{Se}$ system in dimethylformamide (DMF) have confirmed the presence of the corner-bridged oligomeric anions $[\text{Sb}_2\text{Se}_5]^{4-}$ (Raymond *et al.*, 1997), $[\text{Sb}_3\text{Se}_7]^{5-}$, $[\text{Sb}_6\text{Se}_{12}]^{6-}$ and $[\text{Sb}_8\text{Se}_{15}]^{6-}$, only the first of these selenidoantimonate(III) anions has been characterized in the solid state. Both $[\text{Fe}(\text{en})_3]_2\text{Sb}_2\text{Se}_5$ (en = ethylenediamine) (Chen *et al.*, 2000) and $[\text{Mn}(\text{en})_3]_2\text{Sb}_2\text{Se}_5$ (Näther *et al.*, 2003) contain discrete $[\text{Sb}_2\text{Se}_5]^{4-}$ anions comprising two corner-bridged SbSe_3 pyramids. The alternative edge-bridging condensation mode has been established for the *cis*- and *trans*- $[\text{Sb}_2\text{Se}_4]^{2-}$ anions that are present in the crystal structure of $\text{Ba}_4\text{Sb}_4\text{Se}_{11}$ (Cordier *et al.*, 1980), together with discrete SbSe_3^{3-} pyramids and Se_2^{2-} dumb-bells. *cis*- $[\text{Sb}_2\text{Se}_4]^{2-}$ anions have also been characterized in $[\text{K}(2,2,2\text{-crypt})]_2\text{Sb}_2\text{Se}_4$ (2,2,2-crypt is 4,7,13,18,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) (Pell & Ibers, 1996). In contrast, $[\text{K}(2,2,2\text{-crypt})]_2\text{Sb}_2\text{Se}_6$ (Smith *et al.*, 1997) contains cyclic $[\text{Sb}_2\text{Se}_6]^{2-}$ anions in which the component SbSe_3 pyramids are connected through two Se-Se bonds into a six-membered Sb_2Se_4 ring. To our knowledge, only one larger discrete selenidoantimonate(III) has previously been structurally characterized, namely the remarkable $[\text{Sb}_{12}\text{Se}_{20}]^{4-}$ anion in $(\text{Ph}_4\text{P})_4\text{Sb}_{12}\text{Se}_{20}$ (Martin *et al.*, 1994).



We now report the preparation and structure of $\text{Cs}_6\text{Sb}_4\text{Se}_9 \cdot 0.5\text{H}_2\text{O}$, which contains the novel discrete $[\text{Sb}_4\text{Se}_9]^{6-}$ chain anion (Fig. 1) not found by Raymond *et al.*

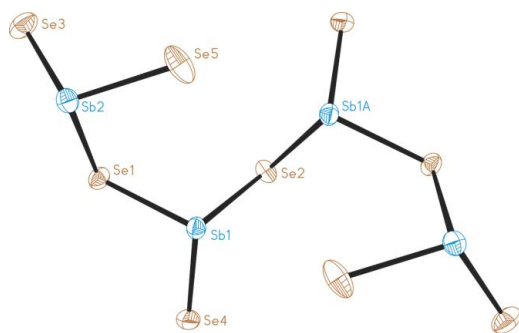


Figure 1

The chain-like $[\text{Sb}_4\text{Se}_9]^{6-}$ anions of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (A) $-x, y, \frac{3}{2} - z$.]

(1997) for the $\text{K}^+/\text{Sb}/\text{Se}$ system. Three caesium selenidoantimonates, CsSbSe_2 (Kanishcheva *et al.*, 1980), CsSb_2Se_4 (Sheldrick & Kaub, 1986) and $\text{Cs}_3\text{Sb}_5\text{Se}_9$ (Sheldrick & Häusler, 1988) had been structurally characterized prior to this study. The last of these phases contains lamellar $[\text{Sb}_5\text{Se}_9]^{3-}$ anions and was prepared under methanolothermal conditions at 453 K (Sheldrick & Wachhold, 1997) from Cs_2CO_3 and Sb_2Se_3 at a very low molar ratio of 1:5.78. A similar temperature (463 K), but a much higher ratio of 2:1, was employed in the present work, leading to the isolation of discrete $[\text{Sb}_4\text{Se}_9]^{6-}$ anions with a lower condensation grade c (Sheldrick & Wachhold, 1998) of 0.444 ($c = y/z$ for anions $[\text{M}_y\text{E}_z]^{m-}$) in comparison with the value of 0.555 for $\text{Cs}_3\text{Sb}_5\text{Se}_9$. The central bridging atom Se2 lies on a crystallographic 2 axis, and bond distances and angles within the corner-bridged SbSe_3 pyramids of the discrete chain anions (Table 1) are typical for tricoordinated Sb^{III} atoms (Sheldrick & Wachhold, 1998). Inspection of Fig. 1 suggests that intermolecular $\text{Sb1A} \cdots \text{Se5}$ interactions [symmetry code: (A) $-x, y, \frac{3}{2} - z$] should be stereochemically favourable, leading to the adoption of a pseudo-trigonal-bipyramidal coordination by the Sb1 atoms. Such hypervalent bonding is typical for selenidoantimonates(III) and is observed, for instance, in the larger discrete $[\text{Sb}_{12}\text{Se}_{20}]^{4-}$ anions of $(\text{Ph}_4\text{P})_4\text{Sb}_{12}\text{Se}_{20}$ (Martin *et al.*, 1994). However, the long $\text{Sb1A} \cdots \text{Se4}$ distance of 3.635 (3) Å clearly rules out any significant contribution in $[\text{Sb}_4\text{Se}_9]^{6-}$.

The cations Cs1–Cs4 are sited in channels between stacks of the $[\text{Sb}_4\text{Se}_9]^{6-}$ anions (Fig. 2) and contain, respectively, eight, six, eight and six Se atoms in their coordination spheres (Table 1). A disordered water O atom was refined with a site occupation factor of 0.5 at the special position $(\frac{1}{2}, 0, 0)$ and can participate in the coordination spheres of Cs2 and/or Cs3. It may be assumed that the methanol solvent, which was not dried prior to use, provided the source of the disordered water.

Experimental

Sb_2Se_3 (480.0 mg, 1.0 mmol) and Cs_2CO_3 (651.6 mg, 2.0 mmol) were heated in a sealed glass tube to 463 K in a CH_3OH /ethylenediamine mixture (4:1 v/v, 0.5 ml). After 2 d, the contents were cooled to room

temperature to afford red crystals of $\text{Cs}_6\text{Sb}_4\text{Se}_9 \cdot 0.5\text{H}_2\text{O}$ in 24% yield. EDX measurements (LEO 1530 Gemini) were in accordance with the expected elemental ratios.

Crystal data

$\text{Cs}_6\text{Sb}_4\text{Se}_9 \cdot 0.5\text{H}_2\text{O}$
 $M_r = 2004.11$
 Monoclinic, $C2/c$
 $a = 10.409$ (2) Å
 $b = 19.064$ (4) Å
 $c = 14.895$ (3) Å
 $\beta = 94.39$ (3)°
 $V = 2947.1$ (10) Å³
 $Z = 4$

$D_x = 4.537$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 17 reflections
 $\theta = 5.0$ – 13.1 °
 $\mu = 22.04$ mm⁻¹
 $T = 293$ (2) K
 Block, red
 $0.14 \times 0.11 \times 0.10$ mm

Data collection

Siemens P4 four-circle diffractometer
 ω scans
 Absorption correction: ψ scan (*XPRED* in *SHELXTL-Plus*; Sheldrick, 1995)
 $T_{\text{min}} = 0.065$, $T_{\text{max}} = 0.108$
 2733 measured reflections
 2563 independent reflections

1796 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.072$
 $\theta_{\text{max}} = 25.0$ °
 $h = 0 \rightarrow 12$
 $k = 0 \rightarrow 22$
 $l = -17 \rightarrow 17$
 3 standard reflections every 97 reflections
 intensity decay: 15%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.067$
 $wR(F^2) = 0.135$
 $S = 1.18$
 2563 reflections
 89 parameters

H atoms not located
 $w = 1/[\sigma^2(F_o^2) + (0.0473P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 1.54$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.72$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cs1–Se5	3.535 (3)	Cs3–Se4	3.677 (3)
Cs1–Se4	3.633 (3)	Cs3–Se5 ⁽ⁱ⁾	3.827 (3)
Cs1–Se1 ⁽ⁱ⁾	3.664 (3)	Cs3–Se1 ^(x)	3.850 (3)
Cs1–Se3 ⁽ⁱ⁾	3.665 (3)	Cs3–Se2	3.855 (3)
Cs1–Se2	3.7807 (19)	Cs3–Se1	4.078 (3)
Cs1–Se4 ⁽ⁱⁱ⁾	3.791 (3)	Cs3–Se3 ⁽ⁱ⁾	4.307 (3)
Cs1–Se3 ⁽ⁱⁱⁱ⁾	3.834 (3)	Cs4–Se5	3.622 (3)
Cs1–Se1 ⁽ⁱⁱⁱ⁾	4.055 (3)	Cs4–Se5 ⁽ⁱⁱⁱ⁾	3.622 (3)
Cs2–Se5 ⁽ⁱⁱ⁾	3.614 (3)	Cs4–Se1 ^(vi)	3.886 (2)
Cs2–Se5	3.614 (3)	Cs4–Se1 ^(xii)	3.886 (2)
Cs2–Se4 ⁽ⁱⁱ⁾	3.740 (3)	Cs4–Se3 ^(vi)	3.905 (3)
Cs2–Se4	3.740 (3)	Cs4–Se3 ^(xii)	3.905 (3)
Cs2–O ^(iv)	3.7536 (8)	Sb1–Se4	2.507 (3)
Cs2–O ^(v)	3.7536 (8)	Sb1–Se2	2.615 (2)
Cs2–Se3 ^(vi)	3.769 (3)	Sb1–Se1	2.626 (3)
Cs2–Se3 ^(vii)	3.769 (3)	Sb2–Se5 ⁽ⁱⁱⁱ⁾	2.517 (3)
Cs3–O ^(viii)	3.5846 (17)	Sb2–Se3	2.522 (3)
Cs3–Se3 ^(ix)	3.670 (3)	Sb2–Se1	2.650 (3)
Cs3–Se4 ^(x)	3.676 (3)		
Se4–Sb1–Se2	98.62 (9)	Se5 ⁽ⁱⁱⁱ⁾ –Sb2–Se1	100.45 (9)
Se4–Sb1–Se1	96.84 (9)	Se3–Sb2–Se1	94.16 (9)
Se2–Sb1–Se1	95.76 (7)	Sb1–Se1–Sb2	97.67 (8)
Se5 ⁽ⁱⁱⁱ⁾ –Sb2–Se3	110.46 (10)	Sb1–Se2–Sb1 ⁽ⁱⁱⁱ⁾	94.14 (11)

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $-x + 1, y, -z + \frac{3}{2}$; (iii) $-x, y, -z + \frac{3}{2}$; (iv) $-x + 1, y, -z + \frac{1}{2}$; (v) $x, y, z + 1$; (vi) $-x, -y, -z + 1$; (vii) $x + 1, -y, z + \frac{1}{2}$; (viii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (ix) $-x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (x) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (xi) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (xii) $x, -y, z + \frac{1}{2}$.

Minimum values of 0.067 and 0.135 were obtained for R and $wR(F^2)$, respectively, on varying the site occupation factor for the disordered water O atom in 0.01 steps in the range 0.5–0.8. The site occupation was, subsequently, set at 0.5 for the final refinement cycles. The H atoms were not located. The highest peak in the final differ-

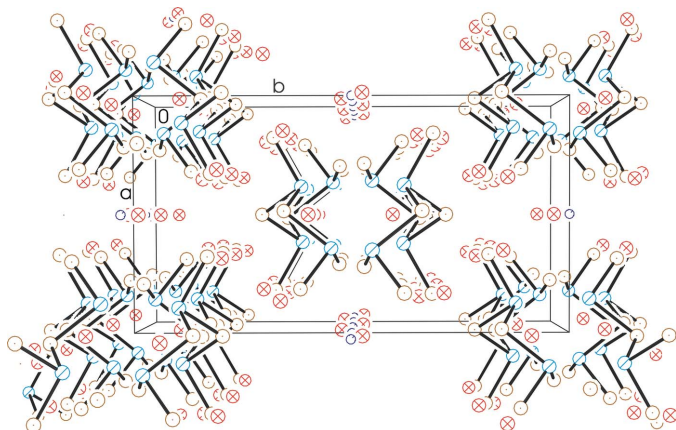


Figure 2
Projection of the structure of (I) perpendicular to the *ab* plane. Atom colour codes: Cs red crossed sphere, Se brown dotted sphere, Sb blue hatched sphere, and O purple open sphere

ence Fourier synthesis is located 1.18 Å from Se3 and the deepest hole is 1.72 Å from Cs1.

Data collection: *R3m/V User's Guide* (Siemens, 1989); cell refinement: *R3m/V User's Guide*; data reduction: *XDISK* (Siemens, 1989);

program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL97*.

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