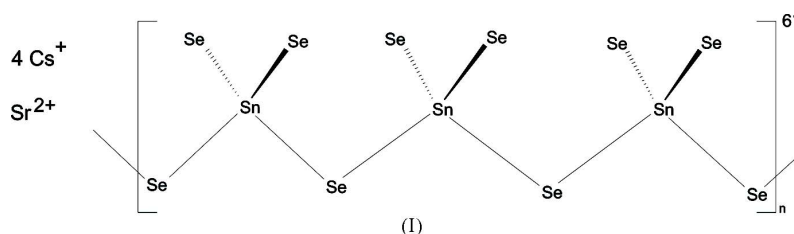


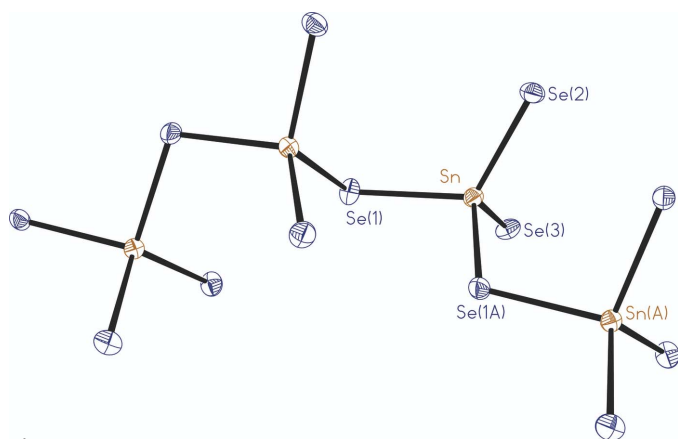
Tobias Van Almsick and
William S. Sheldrick*Lehrstuhl für Analytische Chemie, Ruhr-
Universität Bochum, Universitätsstrasse 150,
44780 Bochum, GermanyCorrespondence e-mail:
william.sheldrick@rub.de

Key indicators

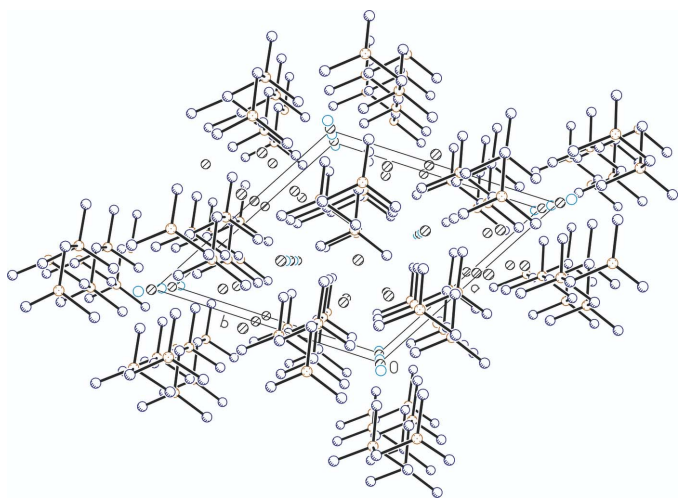
Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(n\text{-Se}) = 0.003\text{ \AA}$
 R factor = 0.036
 wR factor = 0.101
Data-to-parameter ratio = 15.2For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Tetracaesium strontium *catena-nona-*
selenidotristannate(IV)The title compound, $\text{Cs}_4\text{SrSn}_3\text{Se}_9$, contains infinite 'dreier' $[\text{SnSe}_3]^{2-}$ chains consisting of corner-linked SnSe_4 tetrahedra. Whereas the larger independent caesium cations exhibit coordination numbers of 8 and 9, a distorted octahedral environment is observed for the smaller strontium cation.Received 5 September 2005
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Comment

Tetrahedral *ortho*-anions $[\text{SnE}_4]^{4-}$ ($E = \text{S}$ and Se) exhibit a characteristic tendency to condense through corner- or edge-bridging to afford oligomeric or polymeric anions (Krebs, 1983; Sheldrick & Wachhold, 1998). However, whereas edge-bridged ditetrahedral anions $[\text{Sn}_2\text{E}_6]^{4-}$ are readily formed under mildly alkaline solvothermal conditions (Sheldrick & Wachhold, 1997; Sheldrick, 2000), relatively few examples of corner-bridged polymeric $[\text{SnE}_3]^{2-}$ chains of the same formula type are known, and these appear to be restricted to α - and β - Na_2SnSe_3 (Eisenmann & Hansa, 1993*a,b*; Klepp, 1995) for selenidostannates(IV). Discrete ditetrahedral selenidostannate anions $[\text{Sn}_2\text{Se}_6]^{4-}$ have been structurally characterized in the alkali metal phases $A_4\text{Sn}_2\text{Se}_6$ with $A = \text{Na}$ (Krebs & Uhlen, 1987), K (Eisenmann & Hansa, 1993*c*), Rb (Sheldrick & Schaaf, 1994) and Cs (Sheldrick & Braunbeck, 1989).We now report a new example of the corner-bridged $[\text{SnSe}_3]^{2-}$ polyanion in the title compound $\text{Cs}_4\text{SrSn}_3\text{Se}_9$, whose helical $[\text{SnSe}_3]^{2-}$ chains propagate in the $[001]$ direction. Two aspects of this compound are novel: it represents the first quaternary selenidostannate(IV) to contain both an alkali and an alkaline earth counter-cation and the first example of a 'dreier' ($P = 3$, where P , the chain periodicity, is defined as the number of polyhedra within one repeat unit of the linear part of the chain) single chain (Fig. 1) for a polyanion of this type. With the exception of β - Na_2SnSe_3 (Eisenmann & Hansa, 1993*b*; Klepp, 1995), with its remarkable 'sechser' single chains ($P = 6$), all previously known corner-bridged $[\text{GeE}_3]^{2-}$ and $[\text{SnE}_3]^{2-}$ polyanions exhibit a simple 'zweier' periodicity ($P = 2$). The chain conformation in (I) can be gauged by employing Liebau's stretching factor f_s [$f_s = I(\text{chain})/(L_T \cdot P)$] with $I(\text{chain}) =$ chain identity period and $L_T =$ tetrahedron edge length (Liebau, 1985). For $\text{Cs}_4\text{SrSn}_3\text{Se}_9$, the value of 0.825 is


Figure 1

A segment of the 'dreier' single chain $[\text{SnSe}_3]^{2-}$ of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (A) $\frac{5}{3} - x + y, \frac{4}{3} - x, \frac{1}{3} + z$, corresponding to (v) in Table 1.]


Figure 2

Projection of the structure of (I) perpendicular to $[001]$. Atom colour codes: Cs black hatched circles, Sr blue open circles, Se purple semi-hatched circles and Sn orange dotted circles.

similar to that of 0.818 for the 'zweier' chains of $\alpha\text{-Na}_2\text{SnSe}_3$, but much smaller than that of 0.995 in the 'sechser' chains of $\beta\text{-Na}_2\text{SnSe}_3$.

As expected, the bridging Sn–Se1 and Sn–Se1^v distances of, respectively, 2.551 (3) and 2.571 (2) Å are significantly longer than the terminal Sn–Se2 and Sn–Se3 bond lengths [2.467 (2) and 2.472 (2) Å; symmetry code as in Table 1, corresponding to A in Fig. 1]. The Se–Sn–Se angles vary from 99.60 (7)° for Se1–Sn–Se1^v to 118.02 (7)° for Se3–Sn–Se1^v. Fig. 2 depicts a projection of the crystal structure perpendicular to $[001]$. Cs···Se distances in the range 3.661 (2)–4.063 (2) Å are observed for the respectively eight- and ninefold coordinated ions Cs1 and Cs2, with the latter alkali cation positioned on a crystallographic threefold rotation axis. The strontium cation Sr1 also adopts such a special position and exhibits a distorted octahedral coordination, with Sr···Se2 and Sr···Se3 distances of 3.091 (3) and 3.101 (2) Å, respectively.

Experimental

$[\text{Sr}(\text{en})_4]_2(\text{As}_3\text{Se}_6)\text{Cl}$ (en is ethylenediamine; Sheldrick & Kaub, 1985) (300.0 mg, 0.216 mmol) and $\text{Cs}_4\text{Sn}_2\text{Se}_6$ (Sheldrick & Braunbeck, 1989) (268.3 mg, 0.216 mmol) were heated in a sealed glass tube to 463 K in CH_3OH (0.8 ml). After 3 d, the contents were cooled to room temperature to afford black crystals of $\text{Cs}_4\text{SrSn}_3\text{Se}_9$, (I). EDX measurements (LEO 1530 Gemini) were in accordance with the expected elemental ratio.

Crystal data

$\text{Cs}_4\text{SrSn}_3\text{Se}_9$
 $M_r = 1685.97$
 Trigonal, $R\bar{3}$
 $a = 14.528$ (3) Å
 $c = 9.685$ (4) Å
 $V = 1770.4$ (9) Å³
 $Z = 3$
 $D_x = 4.744$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 21 reflections
 $\theta = 4.4\text{--}18.5^\circ$
 $\mu = 25.32$ mm⁻¹
 $T = 293$ (2) K
 Prism, black
 0.11 × 0.10 × 0.09 mm

Data collection

Siemens P4 four-circle diffractometer
 ω scans
 Absorption correction: ψ scan (XPREP in SHELXTL-Plus; Sheldrick, 1995)
 $T_{\min} = 0.075$, $T_{\max} = 0.098$
 945 measured reflections
 792 independent reflections

782 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.044$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -1 \rightarrow 16$
 $k = -17 \rightarrow 1$
 $l = -1 \rightarrow 11$
 3 standard reflections every 97 reflections
 intensity decay: 0.1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.102$
 $S = 1.15$
 792 reflections
 52 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.0779P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 1.52$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.71$ e Å⁻³
 Absolute structure: Flack (1983), 111 Friedel pairs
 Flack parameter: 0.02 (3)

Table 1

Selected geometric parameters (Å, °).

Cs1–Se2 ⁱ	3.661 (2)	Cs2–Se1	4.063 (2)
Cs1–Se2 ⁱⁱ	3.684 (2)	Cs2–Se1 ^{viii}	4.063 (2)
Cs1–Se3 ⁱⁱⁱ	3.777 (2)	Cs2–Se1 ⁱⁱⁱ	4.063 (2)
Cs1–Se2 ^{iv}	3.826 (2)	Sn–Se2	2.467 (2)
Cs1–Se1 ^v	3.836 (3)	Sn–Se3	2.472 (2)
Cs1–Se1	3.848 (2)	Sn–Se1	2.551 (3)
Cs1–Se3 ⁱⁱ	3.849 (2)	Sn–Se1 ^v	2.571 (2)
Cs1–Se3 ^{iv}	3.894 (3)	Sr–Se2 ^{ix}	3.091 (3)
Cs2–Se2 ^{iv}	3.754 (3)	Sr–Se2 ^x	3.091 (3)
Cs2–Se2 ^{vi}	3.754 (3)	Sr–Se2 ^{xi}	3.091 (3)
Cs2–Se2 ^{vii}	3.754 (3)	Sr–Se3 ^{vii}	3.100 (2)
Cs2–Se3	3.862 (3)	Sr–Se3 ^{xiii}	3.101 (2)
Cs2–Se3 ⁱⁱⁱ	3.862 (3)	Sr–Se3 ^{xiii}	3.101 (2)
Cs2–Se3 ^{viii}	3.862 (3)		
Se2–Sn–Se3	110.63 (8)	Se3–Sn–Se1 ^v	118.02 (7)
Se2–Sn–Se1	117.54 (9)	Se1–Sn–Se1 ^v	99.60 (7)
Se3–Sn–Se1	101.43 (8)	Sn–Se1–Sn ⁱ	107.45 (8)
Se2–Sn–Se1 ^v	109.41 (8)		

Symmetry codes: (i) $-y + \frac{4}{3}, x - y - \frac{1}{3}, z - \frac{1}{3}$; (ii) $x + \frac{1}{3}, y + \frac{2}{3}, z - \frac{1}{3}$; (iii) $-y + 1, x - y, z$; (iv) $-x + y + \frac{5}{3}, -x + \frac{4}{3}, z - \frac{2}{3}$; (v) $-x + y + \frac{5}{3}, -x + \frac{4}{3}, z + \frac{1}{3}$; (vi) $-y + \frac{2}{3}, x - y - \frac{2}{3}, z - \frac{2}{3}$; (vii) $x - \frac{1}{3}, y + \frac{1}{3}, z - \frac{2}{3}$; (viii) $-x + y + 1, -x + 1, z$; (ix) $x - \frac{2}{3}, y + \frac{2}{3}, z - \frac{1}{3}$; (x) $-y + \frac{1}{3}, x - y - \frac{1}{3}, z - \frac{1}{3}$; (xi) $-x + y + \frac{2}{3}, -x + \frac{2}{3}, z - \frac{1}{3}$; (xii) $-y + \frac{2}{3}, x - y + \frac{1}{3}, z - \frac{2}{3}$; (xiii) $-x + y + \frac{2}{3}, -x + \frac{4}{3}, z - \frac{2}{3}$.

The highest peak in the final difference Fourier synthesis is located 1.16 Å from Cs1 and the deepest hole 0.47 Å from Cs2.

Data collection: *R3m/V* (Siemens, 1989); cell refinement: *R3m/V*; 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: *XP* in *SHELXTL-Plus* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL97*.

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