Na$_2$SnSe$_3$—A Selenostannate(IV) with Sechser Single Chains

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Red crystals of Na$_2$SnSe$_3$ were synthesized by a fusion reaction of Na$_2$Se, Sn, and Se. Na$_2$SnSe$_3$, oP144, is orthorhombic, space group *Pnma*, with $a = 13.975(4)$ Å, $b = 23.680(6)$ Å, $c = 12.519(3)$ Å; $Z = 24$. The crystal structure was determined from diffractometer data (Ag$K\alpha$) and refined to a conventional R of 0.051 for 2201 reflections with $|F_o|^2 > 3\sigma(|F_o|^2)$ and 190 refined variables. The crystal structure is characterized by infinite anionic chains, $\frac{1}{\infty}$-[SnSe$_3$]$^{2-}$, formed by distorted apex sharing tetrahedra running along [010]. The translation period comprises six tetrahedra. Sn–Se bond lengths are in the range 2.457–2.601 Å with an average of 2.527 Å. Na$^+$-ions are arranged on corrugated layers perpendicular to [010]. They are coordinated to 5–6 chalcogen atoms in irregular configurations. © 1995 Academic Press, Inc.

INTRODUCTION

For a long time the only alkali selenostannates known were the hydrates Na$_4$SnSe$_4$·16H$_2$O (*1*) and Na$_4$Sn$_2$Se$_6$·13H$_2$O (*2*), which had been obtained by the reaction of aqueous Na$_2$Se with SnSe$_2$ under carefully controlled conditions. Recent investigations have, however, revealed the existence of a number of intermediate compounds in the *A*–Sn–Se systems. Thus six ternary phases could be detected and structurally characterized in the K–Sn–Se system. These comprise the selenostannates(IV) K$_4$SnSe$_4$ (*3*), K$_2$SnSe$_3$ (*4*), K$_4$Sn$_3$Se$_8$ (*5*), and K$_2$Sn$_2$Se$_5$ (*6*), the mixed valent compound K$_2$Sn$_4$Se$_8$ (*7*), and K$_6$Sn$_2$Se$_6$ (*4*), where the formal oxidation state + III for Sn is due to a metal–metal bond. Selenostannates of heavier alkali metals, Rb$_2$Sn$_2$Se$_5$ (*8*), Cs$_2$SnSe$_3$ (*9*), and Cs$_2$Sn$_3$Se$_7$ (*10*) were prepared by methanolothermal syntheses under subcritical conditions.

Among these ternary phases the cation rich compounds are characterized by discrete anions with tetrahedrally coordinated Sn atoms. The higher selenostannate(IV) anions may be formally derived by a condensation of SnSe$_4$-tetrahedra via common edges, leading to the bitetrahedral anionic moieties of K$_4$Sn$_2$Se$_6$ (Tl$_4$Ge$_2$S$_6$ (*11*) structure type) or Cs$_4$Sn$_2$Se$_6$, and to the trimeric chain of K$_4$Sn$_3$Se$_8$. In the binuclear complex anions of K$_6$Sn$_2$Se$_6$, which crystallizes with the K$_6$Sn$_2$Te$_6$ (*12*) structure type,

one of the ligands of the tetrahedrally coordinated Sn atoms is a homoatomic neighbor.

In the selenostannates(IV), on passing toward metal-richer stoichiometries, the coordination of Sn changes from tetrahedral to trigonal bipyramidal. Thus Cs$_2$Sn$_3$Se$_7$ is characterized by infinite anionic layers of edge and corner sharing SnSe$_5$-bipyramids. In the isotypic compounds K$_2$Sn$_2$Se$_5$ and Rb$_2$Sn$_2$Se$_5$, which crystallize with the Tl$_2$Sn$_2$S$_5$ (*13*) structure type, chains of edge sharing SnSe$_5$-bipyramids are connected via apical Se atoms to form an infinite anionic framework with large channels hosting the alkali cations. The selenostannate(II,IV) K$_2$Sn$_4$Se$_8$ crystallizes with a unique structure consisting of layers built up by corner-sharing Sn^{IV}Se$_4$-tetrahedra which are connected by Sn(II)-atoms (characterized by a ψ-trigonal bipyramidal coordination) to form an open $\frac{3}{\infty}$-framework.

In continuation of these studies investigations in the system Na–Sn–Se have so far led to the selenostannates(IV) Na$_4$SnSe$_4$ (*3*) and Na$_6$Sn$_2$Se$_7$ (*14*), characterized by discrete tetrahedral anions and isotypic with the corresponding thiostannates (*15–17*). In contrast to the potassium selenostannates(IV) formation of the bitetrahedral anion is attained by corner sharing of the SnSe$_4$-tetrahedra. The same mode of condensation has now been observed with Na$_2$SnSe$_3$, where it yields infinite tetrahedral chains of a surprisingly complex conformation. This compound, which is the first selenostannate characterized by a *pseudo*-one-dimensional structure, is presented below.

EXPERIMENTAL

Synthesis. High purity elements (Na-rods, 99.9%, Sn-powder 99.999%, and Se-pellets 99.999%) were used as starting materials. The synthesis was performed in two steps. In the first the binary compound Na$_2$Se was prepared by reacting the elements (in the molar ratio 2.05 : 1) in carefully dried liquid ammonia using a modified Föppl apparatus (*18*). The reaction product was annealed at 350°C under high-vacuum in order to remove traces of ammonia and Na-metal. A white colored product without

impurities due to polyselenides was obtained by this preparation method. For the synthesis of the ternary compound stoichiometric amounts of Na_2Se, Sn and Se were intimately mixed in an argon dry box, pelleted and sealed into an evacuated silica ampoule. The sample was allowed to react at 850°C for four days, the thermal treatment was completed by a controlled cooling to ambient temperature (cooling rate $2°Ch^{-1}$). Dark red crystals of prismatic shape were isolated from the crushed melt. For the structure determination a specimen with the approximate dimensions $0.13 \times 0.10 \times 0.10$ mm³ was selected and sealed into a well dried glass capillary. Since Na_2SnSe_3 is sensitive to moisture and oxygen all manipulations were performed under an inert argon atmosphere.

Structure Determination. Preliminary crystallographic investigations performed by Weissenberg and precession techniques revealed orthorhombic symmetry. The serial extinctions $0kl$: $k + l \neq 2n$ and $hk0$: $h \neq 2n$ led to $Pnma$ and $Pn2_1a$ as possible space groups.

The intensity data collection was performed on a CAD4-diffractometer (Enraf-Nonius), using graphite monochromated $AgK\alpha$-radiation ($\lambda = 0.5608$ Å) from a sealed tube operated at 50 kV, 26 mA. The intensities were determined by conventional background peak background scans in one octant of the reflection sphere ($2° < 2\theta < 42°$; θ–2θ scan mode, scan width $1.0° + 0.45°$ tan θ) allowing a maximum scan time of 150 s per reflection. Periodically measured control reflections showed only statistical fluctuations in intensity indicating a good crystal and electronic stability. Precise lattice constants were calculated from the angular settings of 24 carefully centered reflections ($30° < 2\theta < 36°$).

The final data set contained 4613 unique reflections, 2201 reflections with $|F_0^2| \geq 3\ \sigma|F_0^2|$ were considered as observed. The statistics of the normalized structure factors showed a pronounced hypercentric distribution. The crystal structure was solved by direct methods (Multan 11/82) (*19*) in the centrosymmetric space group $Pnma$. An E-map calculated from 273 $E \geq 2.03$ phased by 5723 σ^2-relations revealed the locations of the heavy atoms. Na-positions were obtained from subsequent Fourier syntheses. Isotropic refinements converged at an R of 0.075. Refinements with anisotropic temperature factors led to a final R of 0.051 ($R_w = 0.062$). The shift over error ratio of the last cycle of refinement was less than 0.005. A subsequent difference map showed no physically relevant peaks. Crystal data and further details on the structure refinement are given in Table 1. Positional and thermal parameters are listed in Table 2.

All calculations were performed on a DEC Microvax-3520 computer using programs of the Molen crystallographic software package (*20*). Atomic scattering factors for the neutral atoms and coefficients for anomalous dispersion effects were taken from the International Tables

for X-Ray Crystallography (*21*). Absorption effects were taken into account by a spherical correction ($\mu R = 0.5$).

Structure factor tables and a list of anisotropic thermal parameters have been deposited with the Fachinformationzentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information m.b.H., D-76344 Eggenstein Leopoldshafen 2, Germany, under the deposition number C.S.D. 55692.

DISCUSSION

In contrast to Na_2SnO_3 (*22*) and α-Na_2SnS_3 (*23*) which crystallize with NaCl-related structures, the atomic arrangement of Na_2SnSe_3 allows a partial ionic description. It is characterized by the formation of infinite anionic chains of corner sharing $SnSe_4$-tetrahedra, which run parallel to [010] and are separated from each other by Na^+-ions. Infinite, *meta*-silicate like tetrahedral chains with Sn as central atoms have so far only been reported for Tl_2SnS_3 (*24*) and $K_2SnS_3 \cdot 2H_2O$ (*25*). In contrast to these

TABLE 1

Crystal Data and Structure Refinement of Na_2SnSe_3

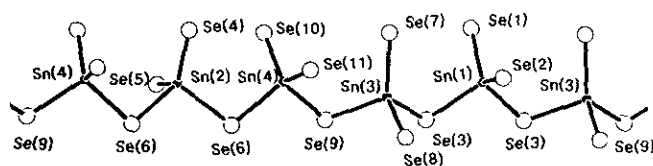|	
Pearson Symbol	$oP144$
$a =$	13.975(4) Å
$b =$	23.680(6) Å
$c =$	12.519(3) Å
Space group	$Pnma$ (No. 62)
$Z =$	24
V (Å³) $=$	4142.7
d_{calc} [gcm⁻³] $=$	3.86
$M_r =$	401.55
$F(000)$	4176
$\mu_{AgK\alpha}$ [cm⁻¹] $=$	103.38
Structure Refinement	
Unique reflections	4613
Observed reflections	2201
Cutoff criterion	$F_0^2 > 3.0\ \sigma(F_0^2)$
Refined variables	190
$R = \Sigma(||F_0| - |F_c||)/\Sigma|F_0|$	0.051
$R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{\frac{1}{2}}$	0.062
$w = [\sigma(F_0^2)^2 + (0.02 \times F_0^2)]^{-\frac{1}{2}}$	
Residual electron density [e Å⁻³]	2.1(2)

FIG. 1. Ball and stick representation of the sechser single $\frac{1}{\infty}$-[SnSe₃]²⁻ chain of Na_2SnSe_3.

TABLE 2

Positional and Thermal Parameters[a] ($\mathring{A}^2 \times 10^2$) for Na_2SnSe_3

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na(1)	0.3997(8)	0.3309(5)	0.5734(9)	2.8(5)	3.7(6)	2.5(5)	0.1(5)	-0.1(5)	-0.2(5)
Na(2)	0.3919(8)	0.4915(5)	0.563(1)	3.0(6)	3.6(7)	3.1(6)	-0.4(5)	0.2(5)	-0.4(5)
Na(3)	0.123(1)	0.4831(6)	0.424(1)	6.1(8)	4.2(7)	5.3(7)	2.8(6)	-2.3(7)	-2.2(6)
Na(4)	0.3868(9)	0.6712(6)	0.6143(9)	3.6(6)	3.9(7)	3.0(6)	0.4(6)	-0.1(5)	0.2(6)
Na(5)	0.172(1)	0.6653(8)	0.381(1)	5.7(8)	12.(1)	3.6(7)	-5.4(8)	-0.3(7)	1.2(8)
Na(6)	0.089(1)	0.3440(8)	0.428(1)	6.5(9)	8.(1)	6.0(9)	0.5(9)	1.5(8)	-2.9(8)
Sn(1)	0.3814(2)	0.75	0.2745(2)	1.3(1)	2.0(1)	1.4(1)	0	-0.0(1)	0
Sn(2)	0.3181(2)	0.25	0.2725(2)	1.7(1)	2.2(1)	1.5(1)	0	-0.4(1)	0
Sn(3)	0.0912(1)	0.41731(8)	0.7193(1)	1.63(7)	2.21(8)	1.35(7)	-0.17(8)	0.04(7)	0.05(8)
Sn(4)	0.3764(1)	0.41632(8)	0.2691(1)	1.53(6)	1.96(7)	1.33(7)	-0.23(8)	-0.12(7)	0.03(8)
Se(1)	0.3077(3)	0.75	0.4539(3)	2.3(2)	3.1(2)	0.9(1)	0	-0.2(2)	0
Se(2)	0.4437(3)	0.25	0.7462(3)	1.3(1)	3.7(1)	1.9(1)	0	0.1(1)	0
Se(3)	0.2003(2)	0.3318(1)	0.6726(2)	1.9(1)	2.5(1)	2.4(1)	0.3(1)	0.8(1)	0.6(1)
Se(4)	0.4426(3)	0.25	0.4111(3)	2.0(2)	3.0(2)	2.1(2)	0	-0.5(2)	0
Se(5)	0.1435(3)	0.25	0.3021(3)	2.1(2)	2.8(2)	2.8(2)	0	-0.2(2)	0
Se(6)	0.1570(2)	0.6666(1)	0.6413(2)	4.1(1)	2.3(1)	1.2(1)	-0.7(1)	0.4(1)	0.2(1)
Se(7)	0.4426(2)	0.5860(1)	0.4122(2)	3.4(1)	3.0(1)	1.5(1)	-0.0(1)	-0.4(1)	0.0(1)
Se(8)	0.0273(2)	0.5870(1)	0.4273(2)	2.1(1)	2.9(1)	2.1(1)	0.0(1)	-0.3(1)	-0.2(1)
Se(9)	0.2021(2)	0.5004(1)	0.6698(2)	2.3(1)	2.4(1)	3.8(1)	-0.5(1)	1.5(1)	-1.0(1)
Se(10)	0.2861(2)	0.4063(1)	0.4379(2)	1.6(1)	3.5(1)	1.4(1)	0.1(1)	0.22(9)	0.3(1)
Se(11)	0.4480(2)	0.5716(1)	0.7286(2)	1.5(1)	3.3(1)	2.1(1)	-0.2(1)	-0.2(1)	0.2(1)

[a] The anisotropic thermal parameters are defined as: $\exp -2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})$.

chains, which are characterized by short translation periods containing one (Tl_2SnS_3) or two ($K_2SnS_3 \cdot 2H_2O$) tetrahedra, the conformation of the selenostannate chain is remarkably complex. It attains identity after a sequence of six tetrahedra and can hence, following the nomenclature proposed by Liebau (26), be classified as a sechser single chain.

A detailed view of the chain, indicating also the atom labelling used for its description, is given in Fig. 1. The chain consists of four crystallographically independent $SnSe_4$-tetrahedra linked together by Se(3), Se(6), and Se(9), respectively. By the mirror planes at $y = \pm \frac{1}{4}$ the

chain is divided into two conformationally different segments of symmetry m: Se(9)–Sn(3)–Se(3)–Sn(1)–Se(3)–Sn(3)–Se(9) (type A, shorthand notation 3–1–3) and Se(9)–Sn(4)–Se(6)–Sn(2)–Se(6)–Sn(4)–Se(9) (type B, shorthand notation 4–2–4). As can be seen from a polyhedral representation (Fig. 2) the mutual torsion of neighboring tetrahedra is small. The edges formed by the bridging atoms are practially colinear in segment A, (∢Se(9)–Se(3)–Se(3) = 179.4°), in other segment they are in a slightly bent arrangement (∢Se(6)–Se(6)–Se(9) = 169.6°); essentially the same angle is formed at the junction of the two segments (∢Se(3)–Se(9)–Se(6) = 169.5°).
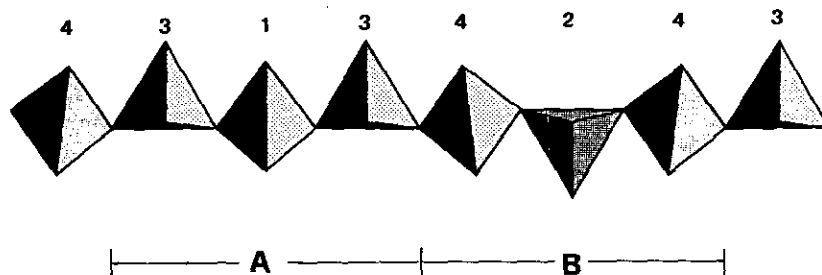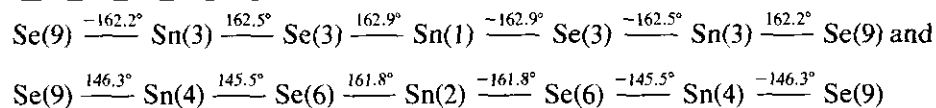

FIG. 2. Polyhedral representation of the sechser single chain of Na_2SnSe_3. The sequence may be divided into two segments (A and B) of symmetry m. Numbers indicate the labeling of the $SnSe_4$-tetrahedra which corresponds to that of their central atoms.

The sequence of torsion angles is

$$Se(9) \xrightarrow{-162.2°} Sn(3) \xrightarrow{162.5°} Se(3) \xrightarrow{162.9°} Sn(1) \xrightarrow{-162.9°} Se(3) \xrightarrow{-162.5°} Sn(3) \xrightarrow{162.2°} Se(9) \text{ and}$$

$$Se(9) \xrightarrow{146.3°} Sn(4) \xrightarrow{145.5°} Se(6) \xrightarrow{161.8°} Sn(2) \xrightarrow{-161.8°} Se(6) \xrightarrow{-145.5°} Sn(4) \xrightarrow{-146.3°} Se(9)$$

for the A and B segments, respectively. Since, disregarding the rather small displacements, the orientation of the tetrahedra 1 and 4 are virtually the same, the chain may be divided into a sequence of five tetrahedra 4–3–1–3–4 with alternating orientations which is interrupted by the tetrahedron 2 which has an orientation approximately inverse to that of tetrahedron 3.

The distortions found in the SnSe₄-tetrahedra are typical for their chain-like arrangement. As can be seen from Table 3 Sn–Se bonds to the bridging Se atoms are by ≈ 0.1 Å longer than those to the terminal Se. The variation among the tetrahedra is rather small, mean values are $d(Sn-Se_b) = 2.586$ Å and $d(Sn-Se_t) = 2.467$ Å. The total average for the Sn–Se bond length is 2.527 Å, in good agreement with the sum of the crystal radii for tetracoordinate Sn(IV) (0.69 Å) and Se (1.84 Å) (27). As might be expected, bond angles follow an inverse trend: The smallest are found between the bridging ($\not\!\!\!\!\times Se_b-Sn-Se_b$: 97.1–102.0°), the largest between the terminal Se-atoms ($\not\!\!\!\!\times Se_t-Sn-Se_t$: 120.5–126.7°). The bond angles on the three bridging selenium atoms are essentially equal ($\not\!\!\!\!\times Sn-Se_b-Sn \approx 102.3°$).

A useful metrical relation for the characterization and comparison of tetrahedral chains $\frac{1}{\infty}AX_{t2}X_{b2/2}$ is the stretching factor $f_s = I/\Sigma d_i$ where I is the identity period and d_i are the lengths of the edges formed by the bridging atoms X_b (28). For the selenostannate chain f_s calculates as 0.995, indicating that the chain is essentially linear. For a complex tetrahedral chain this is a very high value, silicate chains with higher periodicities (>2) are in general characterized by f_s values smaller than 0.9. Based on this indicator the selenostannate chain is conformationally related to the einer single chain of Tl₂SnS₃ (24) ($f_s = 1$, torsion angle = 180°). Among the ternary alkali-IVb-chalcogenides (excluding O) metasilicate type chains are found in the isotypic compounds α-Na₂SiS₃ (29), Na₂GeS₃ (30), and Na₂GeSe₃ (31). The crystal structures of the low temperature form of Na₂SnS₃ (16) and β-Na₂SiS₃ (29), have not been determined. The complex anions in these compound are characterized by a periodicity of 2 (zweier
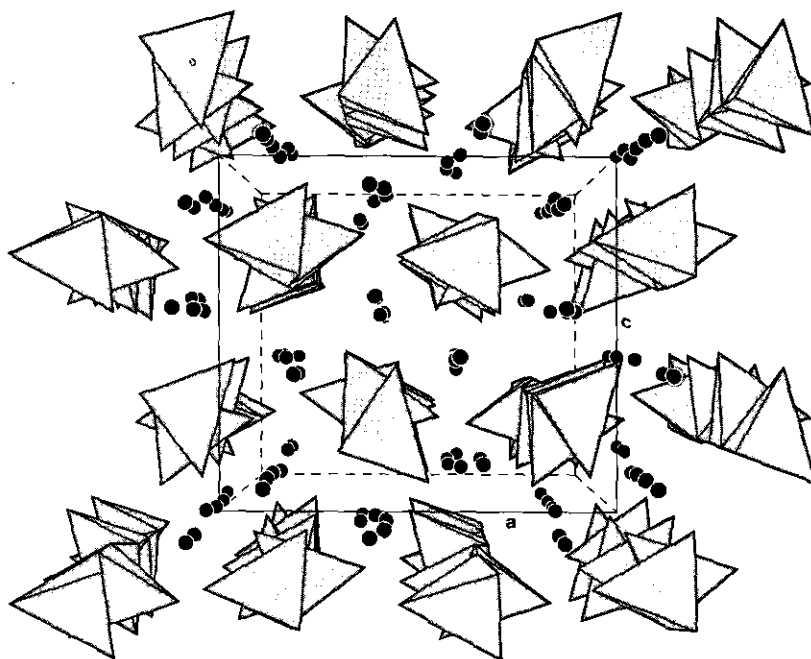

FIG. 3. Projection of the crystal structure of Na₂SnSe₃ along the chain direction. The tetrahedral selenostannate chains are arranged according to a hexagonal rod packing. Na⁺-ions (full circles) are on layers perpendicular to the chain direction and occupy the nodes of distorted 6³-nets.
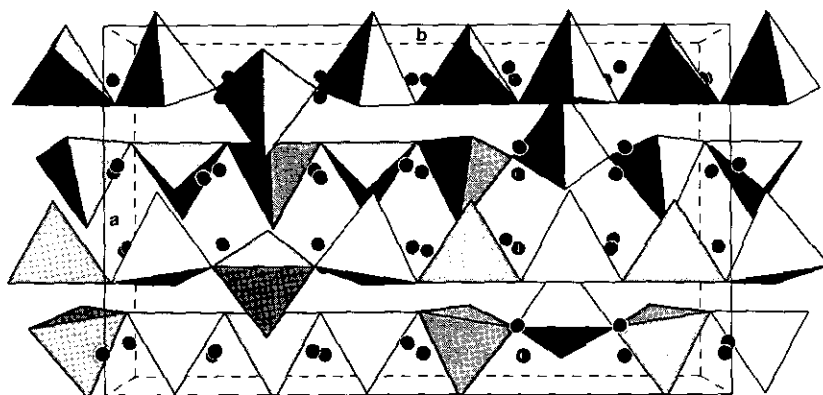
FIG. 4. Projection of the crystal structure of Na_2SnSe_3 along [001]. The origin is in the center of the indicated unit cell.

TABLE 3

Interatomic Distances (Å) and Selected Bond Angles (°) for Na_2SnSe_3

(a) Coordination of the Na^+-ions up to 4.1 Å

Na(1)–Se(4)	2.856(9)	Na(2)–Se(11)	2.921(9)
Na(1)–Se(10)	2.930(9)	Na(2)–Se(10)	2.947(9)
Na(1)–Se(2)	2.953(9)	Na(2)–Se(7)	2.970(9)
Na(1)–Se(7)	2.960(9)	Na(2)–Se(9)	2.981(9)
Na(1)–Se(3)	3.051(9)	Na(2)–Se(7)	3.009(9)
Na(1)–Na(1)	3.83(2)	Na(2)–Na(2)	3.427(2)
Na(1)–Na(2)	3.81(1)	Na(2)–Na(1)	3.81(1)
Na(1)–Na(4)	3.80(1)		
Na(1)–Na(5)	3.97(1)		
Na(3)–Se(8)	2.80(1)	Na(4)–Se(11)	2.888(9)
Na(3)–Se(10)	2.917(9)	Na(4)–Se(1)	2.956(9)
Na(3)–Se(11)	2.94(1)	Na(4)–Se(5)	3.031(9)
Na(3)–Se(8)	3.27(1)	Na(4)–Se(4)	3.045(9)
Na(3)–Se(9)	3.29(1)	Na(4)–Se(6)	3.231(9)
Na(3)–Na(6)	3.33(2)	Na(4)–Se(7)	3.329(9)
		Na(4)–Na(4)	3.73(2)
		Na(4)–Na(1)	3.80(1)
		Na(4)–Na(6)	3.95(1)
		Na(4)–Sn(2)	3.950(9)
Na(5)–Se(8)	2.80(1)	Na(6)–Se(5)	2.83(1)
Na(5)–Se(1)	2.91(1)	Na(6)–Se(8)	2.94(1)
Na(5)–Se(2)	3.07(1)	Na(6)–Se(10)	3.12(1)
Na(5)–Se(3)	3.16(1)	Na(6)–Se(11)	3.24(1)
Na(5)–Se(6)	3.27(1)	Na(6)–Se(3)	3.45(1)
Na(5)–Sn(1)	3.79(1)	Na(6)–Se(6)	3.56(1)
Na(5)–Na(1)	3.97(1)	Na(6)–Sn(2)	4.04(1)
Na(5)–Na(5)	4.01(3)		

(b) Bond lengths and angles of the selenostannate chain

Sn(1)–Se(2)	2.458(3)		Se(3)–Sn(1)–Se(3)	97.05(9)°	
Sn(1)–Se(1)	2.470(3)		Se(1)–Sn(1)–Se(3)	105.35(8)°	2×
Sn(1)–Se(3)	2.585(2)	2×	Se(2)–Sn(1)–Se(3)	112.76(8)°	2×
			Se(1)–Sn(1)–Se(2)	120.70(9)°	
Sn(2)–Se(4)	2.457(4)		Se(6)–Sn(2)–Se(6)	99.2(1)°	
Sn(2)–Se(5)	2.469(4)		Se(5)–Sn(2)–Se(6)	103.18(8)°	2×
Sn(2)–Se(6)	2.592(3)	2×	Se(4)–Sn(2)–Se(6)	110.66(8)°	2×
			Se(4)–Sn(2)–Se(5)	126.4(1)°	

TABLE 3—*Continued*

Sn(3)–Se(7)	2.463(2)		Se(3)–Sn(3)–Se(9)	100.85(7)°
Sn(3)–Se(8)	2.475(2)		Se(3)–Sn(3)–Se(8)	101.15(8)°
Sn(3)–Se(9)	2.579(3)		Se(8)–Sn(3)–Se(9)	104.82(9)°
Sn(3)–Se(3)	2.601(3)		Se(3)–Sn(3)–Se(7)	107.93(9)°
			Se(7)–Sn(3)–Se(9)	112.05(9)°
			Se(7)–Sn(3)–Se(8)	126.68(8)°
Sn(4)–Se(11)	2.471(2)		Se(6)–Sn(4)–Se(9)	101.96(8)°
Sn(4)–Se(10)	2.473(2)		Se(9)–Sn(4)–Se(10)	105.60(9)°
Sn(4)–Se(6)	2.577(3)		Se(6)–Sn(4)–Se(11)	105.99(9)°
Sn(4)–Se(9)	2.577(3)		Se(9)–Sn(4)–Se(11)	109.84(9)°
			Se(6)–Sn(4)–Se(10)	111.43(8)°
			Se(10)–Sn(4)–Se(11)	120.51(8)°
			Sn(1)–Se(3)–Sn(3)	102.35(8)°
			Sn(2)–Se(6)–Sn(4)	102.20(8)°
			Sn(3)–Se(9)–Sn(4)	102.27(8)°

(c) Se–Se contacts up to 4.2 Å

Se(1)–Se(6)	3.720(3)ᵃ	2×	Se(6)–Se(8)	3.743(3)ᵃ
Se(1)–Se(4)	3.877(4)ᵃ		Se(6)–Se(6)	3.948(3)
Se(1)–Se(3)	4.023(3)	2×	Se(6)–Se(9)	4.004(3)
			Se(6)–Se(11)	4.032(3)
Se(2)–Se(3)	4.022(3)ᵃ	2×	Se(6)–Se(10)	4.173(3)
Se(2)–Se(4)	4.195(4)ᵃ			
Se(3)–Se(10)	3.639(2)ᵃ		Se(7)–Se(11)	3.976(3)ᵃ
Se(3)–Se(3)	3.873(4)		Se(7)–Se(9)	4.181(3)
Se(3)–Se(8)	3.921(3)			
Se(3)–Se(9)	3.992(3)		Se(8)–Se(9)	4.005(3)
Se(3)–Se(7)	4.100(3)			
			Se(9)–Se(10)	3.843(3)ᵃ
Se(4)–Se(5)	3.875(4)ᵃ		Se(9)–Se(11)	3.898(3)ᵃ
Se(4)–Se(6)	4.153(3)	2×	Se(9)–Se(10)	4.023(3)
Se(5)–Se(6)	3.966(4)ᵃ	2×	Se(9)–Se(11)	4.132(3)

ᵃ Se–Se contact between the chains

chains). In contrast to the selenostannate chain, they are distinctly corrugated and the neighboring tetrahedra are strongly twisted with respect to each other. Thus for Na₂GeSe₃ (*31*) the stretching factor calculates as 0.859 and the torsion angles are ±174.2° and ±36.9°, respectively.

The projection of the crystal structure along the chain axis (Fig. 3) shows that the arrangement of the chains corresponds to a distorted hexagonal rod packing. As can be seen from Fig. 4 the crystal structure may formally be divided into slightly corrugated layers perpendicular to [010].

The six crystallographically independent Na⁺-ions are coordinated by 5 to 6 chalcogen atoms in irregular and in part distinctly polar configurations. In particular the coordinations of Na(1) and Na(2) may be described as distorted trigonal bipyramids with Na–Se distances ranging from 2.95–3.01 Å. A larger range of distances is found in the coordinations of Na(3) ($d_{Na–Se}$ = 2.80–3.30 Å; distorted square pyramid) and Na(4) ($d_{Na–Se}$ = 2.89–3.33 Å; distorted octahedron). Na(5) and Na(6) have high thermal

displacement parameters (Table 2) which may be attributed to their asymmetrical chalcogen environments. Na(5) has two close ($d_{Na–Se}$ 2.80 and 2.91 Å) and two far ($d_{Na–Se}$ 3.16 and 3.27 Å) neighbors forming the base of a rather flat skew pyramid. Na(6) is coordinated to six Se in a rather distorted octahedral configuration with only three neighbors closer than 3.15 Å. The shortest cation–cation distances are Na(3)–Na(6) = 3.33 Å and Na(2)–Na(2) = 3.427 Å (Table 3).

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