

Methanolothermal Design and Structure of Cesium Polyselenidotellurates $\text{Cs}_4\text{Te}_x\text{Se}_{16-x}$ ($x = 1, 4$) and $\text{Cs}_4\text{Te}_{9.74}\text{Se}_{13.26}$ with Ordered Se/Te Rings and Chains

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The methanolothermal reaction of Cs_2CO_3 with Se in the presence of Bi_2Te_3 at 160°C yields two tellurium-poor mixed polychalcogenides of the general type $\text{Cs}_4\text{Te}_x\text{Se}_{16-x}$. $\text{Cs}_4\text{TeSe}_{15}$ is isostructural with $\text{Cs}_4\text{Se}_{16}$ and crystallizes in the orthorhombic space group *Pbcm* with $a = 10.042(2)$, $b = 14.029(3)$, $c = 19.120(4)$ Å, $Z = 4$, and $V = 2693.6(10)$ Å³. It contains discrete $[\text{TeSe}_{15}]^{4-}$ anions, in which a central Te atom is coordinated in a distorted square-planar manner by three Se_5^{2-} chains, one of which is chelating. $\text{Cs}_2\text{Te}_2\text{Se}_6$ crystallizes in the monoclinic space group *P2₁/c* with $a = 7.436(1)$, $b = 6.771(1)$, $c = 13.489(3)$ Å, $\beta = 95.55(3)^\circ$, $Z = 2$, and $V = 676.0(2)$ Å³ and is isostructural with Cs_2Te_8 . If distances longer than 2.90 Å are ignored, the anionic structure may be described as a discrete $[\text{Te}_2\text{Se}_6]^{2-}$ chain in which the Te atoms adopt the third and sixth positions. Individual chains are connected through Te ... Se interactions of lengths 2.922(2) and 3.244(1) Å into sheets. When Sb_2Te_3 is employed in place of Bi_2Te_3 , reaction of Cs_2CO_3 with Se yields $\text{Cs}_4[\text{TeSe}_3]_2 \cdot \text{Te}_3\text{Se}_3 \cdot 1.5(\text{Te}_{3.21}\text{Se}_{2.79})$ in which pyramidal $[\text{TeSe}_3]^{2-}$ anions and respectively ordered and disordered $\text{Te}_x\text{Se}_{6-x}$ rings are connected through secondary Te ... Se bonds into polymeric layers. $\text{Cs}_4\text{Te}_{9.74}\text{Se}_{13.26}$ crystallizes in the rhombohedral space group *R $\bar{3}$* with $a = b = 12.022(2)$, $c = 44.072(9)$ Å, $Z = 6$, and $V = 5516(2)$ Å³. © 1997 Academic Press

INTRODUCTION

Technological interest in the design of zeotype solid-state materials with multifunctional tailor-made properties has stimulated current research into “chimie douce” synthetic approaches at intermediate temperatures, including molten flux and solventothermal techniques (1–3). Superheated strongly polarizing solvents such as water, methanol, and amines at temperatures in the range 110–200°C provide reaction conditions adequate to greatly enhance solubility, diffusion, and crystallization but still mild enough to

leave molecular building blocks such as chains and rings intact to participate in the construction of open sheet and framework chalcogenidometalates (3).

Aqueous or methanolic solutions of alkali metal carbonates induce disproportionation of S, Se, and Te to oxoanions (4) and polychalcogenides E_x^{2-} , thereby affording a convenient source of the latter chainlike oligomers for mild hydro- or methanolothermal synthesis. Furthermore, binary polychalcogenides themselves can be isolated from such media in the presence of suitable cations. For instance, reaction of Cs_2CO_3 with Se in superheated methanol at 160°C leads to the formation of $\text{Cs}_4\text{Se}_{16}$, in which the Se_{16}^{4-} anion consists of a central Se atom coordinated in a severely distorted square-planar manner by one chelating and two terminal Se_5^{2-} chains (5). Under similar methanolothermal conditions (3), substitution of Te for Se as the chalcogen reaction partner affords the known tellurides Cs_2Te_3 and Cs_2Te_5 (6). However, we have recently demonstrated that fine control of both redox potential and temperature allows access to a new family of very tellurium-rich alkali metal (A) tellurides $A_x\text{Te}_y$ with $x/y \leq 1/6$. Thus RbTe_6 (7) may be prepared by methanolothermal reaction of Rb_2CO_3 with Te in the presence of Ge at 160°C , and the structurally related novel metastable phases $\text{Cs}_2\text{Te}_{13}$, $\text{Cs}_4\text{Te}_{28}$ (8), and $\text{Cs}_3\text{Te}_{22}$ (9) can be obtained, together with Cs_2Te_5 , by heating As_2Te_3 in a methanolic solution of Cs_2CO_3 to temperatures in the respective ranges 150–160, 170–180, and 190–220°C. Metallic properties have been predicted for the unique planar ${}_\infty^2[\text{Te}_6^{3-}]$ sheets of $\text{Cs}_3\text{Te}_{22}$ on the basis of extended-Hückel MO calculations (10).

We have also reported the preparation of the selenido-metalates (V) $A_3M\text{Se}_4$ ($A = \text{Rb}, \text{Cs}$; $M = \text{As}, \text{Sb}$) (11) by treatment of $A_2\text{CO}_3$ with $M_2\text{Se}_3$ and Se in superheated methanol. Lowering the $\text{Rb}_2\text{CO}_3:\text{As}_2\text{Se}_3$ ratio allows the isolation of $\text{Rb}_3\text{AsSe}_4 \cdot 2\text{Se}_6$, and the isostructural phase $\text{Cs}_3\text{AsSe}_4 \cdot 2\text{Cs}_2\text{As}_2\text{Se}_4 \cdot 6\text{Te}_4\text{Se}_2$ with disordered six-membered $\text{Te}_x\text{Se}_{6-x}$ rings may be obtained by methanolothermal reaction of Cs_2CO_3 with As_2Te_3 and Se (12). These

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findings and our discovery of the new class of very tellurium-rich alkali metal tellurides prompted us to investigate the possibility of designing mixed selenides/ tellurides of the type $\text{Cs}_4\text{Te}_x\text{Se}_y$. Böttcher has reported the isostructural pair Rb_2Te_5 (13) and Rb_2TeSe_4 (14), which contain respectively edge-bridged square-planar TeTe_4 and TeSe_4 building units and reflect, thereby, the increased propensity of the heavier Group 16 element to increase its coordination number above 2. An analogous selective introduction of Te at the fourfold coordination position in $\text{Cs}_4\text{Se}_{16}$ should provide $\text{Cs}_4\text{TeSe}_{15}$. Alternatively, an Se/Te substitution at all twofold coordination sites in Cs_2Te_8 (15) would generate the tellurium-richer phase $\text{Cs}_2\text{Te}_2\text{Se}_6$.

We now present the preparation of these mixed cesium polychalcogenides by methanolothermal reaction of Cs_2CO_3 with Se in the presence of Bi_2Te_3 as a low release velocity source of Te. Replacement of Bi_2Te_3 with Sb_2Te_3 leads to an acceleration in tellurium solubilization and the formation of a tellurium-richer phase $\text{Cs}_4\text{Te}_{9.74}\text{Se}_{13.26}$, $\text{Cs}_4(\text{TeSe}_3)_2 \cdot \text{Te}_3\text{Se}_3 \cdot 1.5(\text{Te}_{3.21}\text{Se}_{2.79})$, that contains the first example of an ordered mixed Te/Se ring to be characterized in the solid state.

EXPERIMENTAL

Syntheses

Cs₄TeSe₁₅ and Cs₂Te₂Se₆. Bi_2Te_3 was pulverized prior to use and employed in a microcrystalline form (crystal dimensions ≤ 0.1 mm). A glass tube (~ 10 -ml capacity) containing 0.165 g (0.51 mmol) of Cs_2CO_3 , 0.405 g (0.51 mmol) of Bi_2Te_3 , and 0.365 g (4.62 mmol) of Se in 2.6 ml of methanol was sealed under vacuum and heated to 160°C at a rate of $10^\circ\text{C} \cdot \text{h}^{-1}$. After 96 h at this temperature, the glass tube was allowed to cool to 20°C at $2^\circ\text{C} \cdot \text{h}^{-1}$. Bunches of black platelike crystals of $\text{Cs}_4\text{TeSe}_{15}$ and black prismatic crystals of $\text{Cs}_2\text{Te}_2\text{Se}_6$ were separated manually and washed with methanol to provide the products in respectively 11 and 26% yield (based on Cs_2CO_3).

Cs₄Te_{9.74}Se_{13.26}. Sb_2Te_3 was pulverized prior to use. A glass tube (~ 10 -ml capacity) containing 0.163 g (0.50 mmol) of Cs_2CO_3 , 0.322 g (0.51 mmol) of Sb_2Te_3 , and 0.241 g (3.05 mmol) of Se in 1.2 ml of methanol was sealed under vacuum and heated to 200°C at a rate of $10^\circ\text{C} \cdot \text{h}^{-1}$. After 72 h at this temperature, the glass tube was cooled to 20°C at $2^\circ\text{C} \cdot \text{h}^{-1}$. Bunches of large black hexagonal prisms were separated manually and washed with methanol to afford $\text{Cs}_4\text{Te}_{9.74}\text{Se}_{13.26}$ in 41% yield (based on Cs_2CO_3).

X-Ray Structural Analysis

All compounds were examined by X-ray powder diffraction to establish phase purity. Calculated and observed XRD patterns were found to match well. Crystal and refine-

TABLE 1
Crystal and Refinement Data for $\text{Cs}_4\text{TeSe}_{15}$ (1), $\text{Cs}_2\text{Te}_2\text{Se}_6$ (2), and $\text{Cs}_4\text{Te}_{9.74}\text{Se}_{13.26}$ (3)

	1	2	3
Space group	<i>Pbcm</i>	<i>P2₁/c</i>	<i>R$\bar{3}$</i>
<i>a</i> (Å)	10.042(2)	7.436(1)	12.022(2)
<i>b</i> (Å)	14.029(3)	6.771(1)	12.022(2)
<i>c</i> (Å)	19.120(4)	13.489(3)	44.072(9)
α (°)	90	90	90
β (°)	90	95.55(3)	90
γ (°)	90	90	120
<i>V</i> (Å ³)	2693.6(10)	676.0(2)	5516(2)
<i>Z</i>	4	2	6
<i>M</i>	1843.6	994.8	2821.6
<i>F</i> (000)	3128	836	7064
<i>D</i> _{calc} (g · cm ⁻³)	4.55	4.89	5.10
Radiation	MoK α	MoK α	MoK α
μ (mm ⁻¹)	26.69	25.72	24.63
Crystal size (mm)	0.30 × 0.21 × 0.20	0.26 × 0.24 × 0.22	0.31 × 0.25 × 0.25
Absorption corr	ψ scan	ψ scan	ψ scan
Max/min trans	0.020/0.002	0.028/0.002	0.005/0.001
$2\theta_{\text{max}}$ (°)	55°	60°	60°
<i>hkl</i> range	0/13, 0/18, 0/24	0/10, 0/9, -18/18	0/14, 0/14, -61/61
Independent refl	3134	1965	3552
$R[I > 2\sigma(I)]^a$	0.078	0.043	0.068
wR2 [all data] ^b	0.115	0.094	0.126

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$$

ment data are listed for $\text{Cs}_4\text{TeSe}_{15}$, $\text{Cs}_2\text{Te}_2\text{Se}_6$, and $\text{Cs}_4\text{Te}_{9.74}\text{Se}_{13.26}$ in Table 1. Unit cell constants were obtained from the least-squares fit to the settings for 25 reflections ($25^\circ \leq 2\theta \leq 30^\circ$) centered on a Siemens P4 diffractometer. Intensity data were collected on this instrument in the ω mode at 293 K. Significant deviations in intensity were not observed for three selected reflections that were monitored during the course of data collection for each of the compounds. Semiempirical absorption corrections were performed on the basis of ψ scans for nine chosen reflections with high χ values. After structure solution with SHELXS-86 (16), positional parameters and anisotropic temperature factors were refined against F_o^2 with SHELXL-93 (17). The terminal reliability index wR2 in Table 1 is defined as $[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ with weights given by $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$ with $P = [\max(F_o^2, 0) + 2F_c^2]/3$. The crystal lattice of $\text{Cs}_4\text{Te}_{9.74}\text{Se}_{13.26}$ contains two crystallographically independent mixed Te/Se six-membered rings, the first of which is ordered [Te(3)/Se(3)] with C_3 symmetry and the second disordered [Te/Se(4), Te/Se(5), Te(6)] with C_i symmetry. Refinement of the site occupation factors (sof's) for mixed occupation of positions Te/Se(4), Te/Se(5), and Te(6) gave a minimal wR2 value for sof's 0.19/0.81, 0.42/0.58, and 1.0/0.0, corresponding to the formulation $\text{Te}_{3.21}\text{Se}_{2.79}$. Resolution of the Te/Se(4) and Te/Se(5) positions was not possible. Atom coordinates with

TABLE 2
Atom Positional Parameters with Equivalent Isotropic
Temperature Factors U_{eq} ($\text{\AA}^2 \times 10^3$)^a

Atom	x/a	y/b	z/c	U_{eq}
Cs₄TeSe₁₅				
Cs(1)	0.9656(3)	0.1140(2)	0.75	49(1)
Cs(2)	0.6532(3)	-0.1116(2)	0.75	59(1)
Cs(3)	-0.1231(3)	0.25	0.0	48(1)
Cs(4)	0.4056(3)	0.25	0.0	61(1)
Te(1)	0.4556(3)	0.1171(2)	0.75	54(1)
Se(1)	0.2901(3)	0.0701(2)	0.8489(1)	46(1)
Se(2)	0.3135(3)	-0.0957(2)	0.8467(1)	53(1)
Se(3)	0.1812(5)	-0.1394(3)	0.75	59(1)
Se(4)	0.6588(3)	0.1637(2)	0.8569(1)	54(1)
Se(5)	0.6063(3)	0.0357(2)	0.9309(1)	49(1)
Se(6)	0.8136(4)	-0.0120(2)	0.9768(1)	58(1)
Se(7)	0.9318(3)	-0.0783(2)	0.8837(1)	55(1)
Se(8)	0.8637(3)	-0.2365(2)	0.8721(1)	56(1)
Cs₂Te₂Se₆				
Cs(1)	0.1394(1)	0.8931(1)	0.3568(1)	46(1)
Te(1)	0.3756(1)	0.0605(1)	0.1242(1)	36(1)
Se(1)	0.8833(2)	0.9056(1)	0.0315(1)	41(1)
Se(2)	0.4494(2)	0.6963(1)	0.0817(1)	38(1)
Se(3)	0.6550(2)	0.0052(1)	0.2896(1)	42(1)
Cs₄Te_{9.74}Se_{13.26}				
Cs(1)	-0.0237(1)	0.4493(1)	0.0534(1)	58(1)
Cs(2)	0.0	0.0	0.1334(1)	54(1)
Te(1)	0.3333	0.6667	0.1215(1)	42(1)
Se(1)	0.2218(2)	0.7703(1)	0.0968(1)	52(1)
Te(2)	0.3333	0.6667	0.0226(1)	45(1)
Se(2)	0.2280(2)	0.4483(1)	-0.0008(1)	54(1)
Se(3)	0.1900(1)	0.1769(1)	0.0647(1)	47(1)
Te(3)	0.0155(1)	0.2000(1)	0.0378(1)	47(1)
Se(4)/Te(4) ^b	-0.1620(1)	0.5359(1)	0.1295(1)	50(1)
Se(5)/Te(5) ^c	-0.0507(1)	0.6799(1)	0.2119(1)	51(1)
Te(6)	0.0511(1)	0.7029(1)	0.1557(1)	47(1)

^a U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

^bSite occupation factors 0.81/0.19.

^cSite occupation factors 0.58/0.42.

equivalent isotropic temperature factors are listed for Cs₄TeSe₁₅, Cs₂Te₂Se₆, and Cs₄Te_{9.74}Se_{13.26} in Table 2, and bond lengths and angles are given in Tables 3–5.

RESULTS AND DISCUSSION

Methanolothermal Synthesis

In the absence of the effectively insoluble tellurides M_2Te_3 ($M = Sb, Bi$), methanolothermal reaction of Cs₂CO₃ and Se leads to disproportionation of the chalcogen and isolation of the polyselenide Cs₄Se₁₆ (5). In contrast to As₂Te₃ (8, 9), no reaction is observed when a methanolic solution of Cs₂CO₃ is heated to 240°C in the presence of M_2Te_3 ($M = Sb, Bi$). Whereas As₂Te₃

TABLE 3
Bond Lengths (\AA) and Angles ($^\circ$) in Cs₄TeSe₁₅ with Analogous
Parameters in the Isostructural Compound Cs₃Se₁₆ (5) Given in
Square Brackets

Te(1)–Se(1)	2.602(3)	[2.425(4)]
Te(1)–Se(4)	2.962(4)	[2.989(4)]
Se(1)–Se(2)	2.338(4)	[2.356(4)]
Se(2)–Se(3)	2.358(4)	[2.344(4)]
Se(4)–Se(5)	2.345(4)	[2.326(4)]
Se(5)–Se(6)	2.356(5)	[2.356(4)]
Se(6)–Se(7)	2.333(4)	[2.339(5)]
Se(7)–Se(8)	2.333(5)	[2.314(4)]
Se(1)⋯Se(8')	3.154(4)	[3.132(4)]
Se(1)–Te(1)–Se(1a)	93.2(2)	[97.0(2)]
Se(1)–Te(1)–Se(4)	99.7(1)	[90.2(1)]
Se(1)–Te(1)–Se(4a)	176.0(1)	[172.4(2)]
Se(4)–Te(1)–Se(4a)	87.3(1)	[82.4(2)]
Te(1)–Se(1)–Se(2)	100.1(1)	[100.9(2)]
Se(1)–Se(2)–Se(3)	102.5(2)	[101.4(2)]
Se(2)–Se(3)–Se(2a)	103.3(2)	[102.7(2)]
Te(1)–Se(4)–Se(5)	95.3(1)	[95.2(1)]
Se(4)–Se(5)–Se(6)	104.1(2)	[105.1(2)]
Se(5)–Se(6)–Se(7)	106.2(1)	[105.5(2)]
Se(6)–Se(7)–Se(8)	107.6(2)	[108.2(2)]
Se(7)–Se(8)⋯Se(1')	167.3(2)	[166.3(2)]
Te(1)–Se(1)⋯Se(8')	101.4(1)	[103.4(1)]
Se(2)–Se(1)⋯Se(8')	155.2(2)	[152.3(2)]

affords a deep brown polytelluride solution from which the tellurium-rich tellurides Cs₂Te₁₃, Cs₄Te₂₈, and Cs₃Te₂₂ can be isolated, the solvent remains colorless for the heavier Group 15 tellurides.

TABLE 4
Bond Lengths (\AA) and Angles ($^\circ$) in Cs₂Te₂Se₆ with Analogous
Parameters in the Isostructural Compound Cs₂Te₃ (15) Given in
Square Brackets

Te(1)–Se(1)	2.718(2)	[2.923(2)]
Te(1)–Se(2)	2.603(1)	[2.839(1)]
Te(1)–Se(3a)	2.922(2)	[3.135(2)]
Te(1)–Se(3b)	3.244(1)	[3.378(2)]
Se(1)–Se(1')	2.378(2)	[2.764(2)]
Se(2)–Se(3)	2.357(2)	[2.754(1)]
Se(1)–Te(1)–Se(2)	93.34(4)	[93.5(1)]
Se(1)–Te(1)–Se(3a)	177.41(4)	[176.5(1)]
Se(1)–Te(1)–Se(3b)	97.47(3)	[95.4(1)]
Se(2)–Te(1)–Se(3a)	84.09(4)	[83.6(1)]
Se(2)–Te(1)–Se(3b)	169.17(4)	[170.8(1)]
Se(3a)–Te(1)–Se(3b)	85.09(3)	[87.4(1)]
Te(1)–Se(1)–Se(1')	99.50(6)	[95.9(1)]
Te(1)–Se(2)–Se(3)	105.47(5)	[103.1(1)]
Te(1)–Se(3a)–Se(2a)	103.40(5)	[101.7(1)]
Te(1)–Se(3b)–Se(2b)	101.87(5)	[101.0(1)]
Te(1)–Se(3a)–Te(1a)	108.88(4)	[111.1(1)]

TABLE 5
Bond Lengths (Å) and Angles (°) in $\text{Cs}_4\text{Te}_9.74\text{Se}_{13.26}$

Te(1)–Se(1)	2.497(2)	Te(2)–Se(2)	2.491(2)
Te(3)–Se(3)	2.544(2)	Te(3)–Se(3')	2.572(2)
Se(1)–Te(1)–Se(1')	104.15(7)	Se(2)–Te(2)–Se(2')	102.38(7)
Se(3)–Te(3)–Se(3')	96.87(7)	Te(3)–Se(3)–Te(3')	103.33(7)

A relatively low solubility of the components is generally desirable for solventothermal techniques; the molecular building blocks (e.g., Se_x^{2-} chains) should be easily removable from solution by their participation in the construction of polymeric anions at the site of crystallization (3). Our present results demonstrate that Bi_2Te_3 is able to release tellurium at the very low rate necessary to enable the formation of the tellurium-poor polychalcogenides $\text{Cs}_4\text{TeSe}_{15}$ and $\text{Cs}_2\text{Te}_2\text{Se}_6$ under methanolothermal conditions at 160°C. These phases are isostructural with $\text{Cs}_4\text{Se}_{16}$ (5) and Cs_2Te_8 (15) and respectively 1/16 and 1/4 of their chalcogen sites, now occupied by Te atoms, exhibit a square-planar coordination geometry. Support for a mechanism involving the slow release of tellurium at the site of crystallization is provided by our observation of product growth on the surface of larger Bi_2Te_3 crystals (dimensions 0.1–1.0 mm) when these are employed for the methanolothermal synthesis. The selective incorporation of Te atoms at the chalcogen sites with high coordination numbers in $\text{Cs}_4\text{TeSe}_{15}$ and $\text{Cs}_2\text{Te}_2\text{Se}_6$ suggests that the strategy of slow tellurium release from effectively insoluble tellurides could open a wide field for the solventothermal design of chalcogenidometalates.

Sb_2Te_3 exhibits, as expected, an increased solubilization velocity in methanol in comparison to Bi_2Te_3 and this allows the isolation of a tellurium-rich polychalcogenide $\text{Cs}_4\text{Te}_9.74\text{Se}_{13.26}$. The higher Te/Se ratio now favors the formation of pyramidal TeSe_3^{2-} anions and mixed Te/Se six-membered rings, Te_3Se_3 and $\text{Te}_{3.21}\text{Se}_{2.79}$, rather than the Se_5^{2-} chainlike units in $\text{Cs}_4\text{TeSe}_{15}$ or the $[\text{Te}_2\text{Se}_6]^{2-}$ chains in $\text{Cs}_2\text{Te}_2\text{Se}_6$.

Structure of $\text{Cs}_4\text{TeSe}_{15}$

The structure of the C_s symmetric $[\text{TeSe}_{15}]^{4-}$ anionic units in $\text{Cs}_4\text{TeSe}_{15}$ is depicted in Fig. 1; bond lengths and angles are contained in Table 3. Incorporation of the heavier Group 16 element leads to a marked reduction in the degree of distortion of the square-planar coordination geometry at the central atom in $[\text{TeSe}_{15}]^{4-}$ in comparison to Se_{16}^{4-} in the isostructural compound $\text{Cs}_4\text{Se}_{16}$ (5). For instance, the difference between the *trans* sited distances Te(1)–Se(1) and Te(1)–Se(4a) is 0.204 Å smaller in

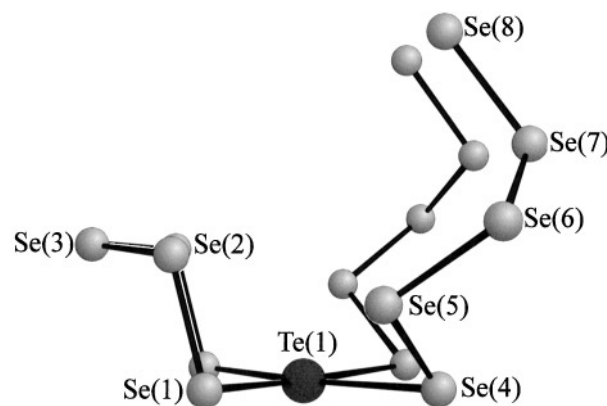


FIG. 1. The $[\text{TeSe}_{15}]^{4-}$ anion in $\text{Cs}_4\text{TeSe}_{15}$.

$[\text{TeSe}_{15}]^{4-}$ than for the analogous bonds in Se_{16}^{4-} and the angle of 93.2(2)° at Te(1) within the six-membered TeSe_5 ring is much closer to the idealized value (90°) than that of 97.0(2)° in the polyselenide. As a result of this concomitant bond lengthening and angle narrowing at Te(1), the remaining angles in the chair-shaped Se_5Te ring of $[\text{TeSe}_{15}]^{4-}$ lie in a range [100.1(1)–103.3(2)°] similar to those in the Se_6 ring of Se_{16}^{4-} [100.9(2)–102.7(2)°]. The Se_5^{2-} chains in these isostructural compounds adopt a *trans* conformation, as previously observed for the isolated anions in Rb_2Se_5 (18), Cs_2Se_5 (14) and $[\text{Ph}_4\text{P}]_2\text{Se}_5$ (19).

Literature examples of square-planar TeSe_4 units are restricted to Rb_2TeSe_4 (14) with $1/2[\text{TeSe}_4^{2-}]$ chains and the spirocyclic anions $[\text{TeSe}_{10}]^{2-}$ in $[\text{K}(2,2,2\text{-crypt})_2]\text{TeSe}_{10}$ and $[\text{Ba}(2,2,2\text{-crypt})(\text{en})]\text{TeSe}_{10} \cdot 0.5 \text{ en}$ (21). Te–Se distances in the six-membered Se_5Te rings of the isolated $[\text{TeSe}_{10}]^{2-}$ anions lie in the narrow range 2.805–2.824 Å and may be regarded as representative for an undistorted square-planar environment in a selenidotellurate(II). The anion dimensions in $\text{Cs}_4\text{TeSe}_{15}$ are, therefore, in accordance with a structure intermediate between the extreme formulations as an isolated Se_5Te ring with interactions to two discrete Se_5^{2-} chains and a selenidotellurate(II) $[\text{TeSe}_{15}]^{4-}$ with a central Te(II) atom. As for $\text{Cs}_4\text{Se}_{16}$, the chains and $\text{Cs}_4\text{TeSe}_{15}$ rings are connected through weak Se(1)⋯Se(8') interactions of length 3.154(4) Å into the polymeric structure depicted in Fig. 2. On including these contacts, the selenium atoms Se(1) exhibit a severely distorted T-shaped coordination geometry with an Se(2)–Se(1)⋯Se(8') angle of 155.2(2)°. The structure directing role of the alkali cations in the formation of $\text{Cs}_4\text{TeSe}_{15}$ is emphasized by Fig. 3, which demonstrates the coordination of Cs(2) by no less than 9 chalcogen atoms from a single $[\text{TeSe}_{15}]^{4-}$ unit. Whereas Cs(1) also displays 10 nearest neighbors (from four independent $[\text{TeSe}_{15}]^{4-}$ units), the remaining independent cations Cs(3) and Cs(4) exhibit a coordination number of 12 involving respectively six and four $[\text{TeSe}_{15}]^{4-}$ units.

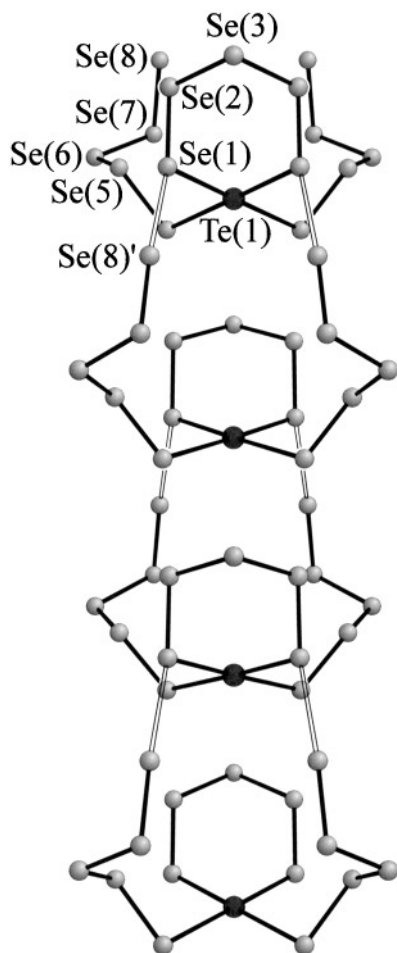


FIG. 2. Connection of individual $[\text{TeSe}_{15}]^{4-}$ anions in $\text{Cs}_4\text{TeSe}_{15}$ through $\text{Se}(1)\cdots\text{Se}(8')$ interactions [$3.154(4)\text{ \AA}$] into $\frac{1}{6}[\text{TeSe}_{15}^{4-}]$ chains in direction $[010]$ (open bonds).

Structure of $\text{Cs}_2\text{Te}_2\text{Se}_6$

$\text{Cs}_2\text{Te}_2\text{Se}_6$ crystallizes in the monoclinic space group $P2_1/c$ and is isostructural with Cs_2Te_8 (15). On ignoring Se–Se and Te–Se interactions longer than 2.90 \AA , the anionic part of the crystal structure can be described as an isolated $[\text{Te}_2\text{Se}_6]^{2-}$ chain in which the tellurium atoms adopt the third and sixth positions. As depicted in Fig. 4, these chains exhibit crystallographic C_i symmetry with a central planar $(\text{TeSe})_2$ unit. Individual $[\text{Te}_2\text{Se}_6]^{2-}$ chains are linked through longer $\text{Te}(1)\cdots\text{Se}(3)$ interactions of length $2.922(2)$ and $3.244(1)\text{ \AA}$ into $\frac{2}{\infty}[\text{Te}_2\text{Se}_6^{2-}]$ sheets (Fig. 5). This connectivity pattern is directed by the large alkali cations Cs^+ that adopt positions central to the sizeable $12\text{-membered Te}_4\text{Se}_8$ rings of neighboring anionic layers. Such cavities are bordered by ladders of smaller fused five-membered Te_2Se_3 rings. When the longer Te–Se bonds are included, it is apparent from Fig. 5 that the methanolothermal synthesis of $\text{Cs}_2\text{Te}_2\text{Se}_6$ leads to the selec-

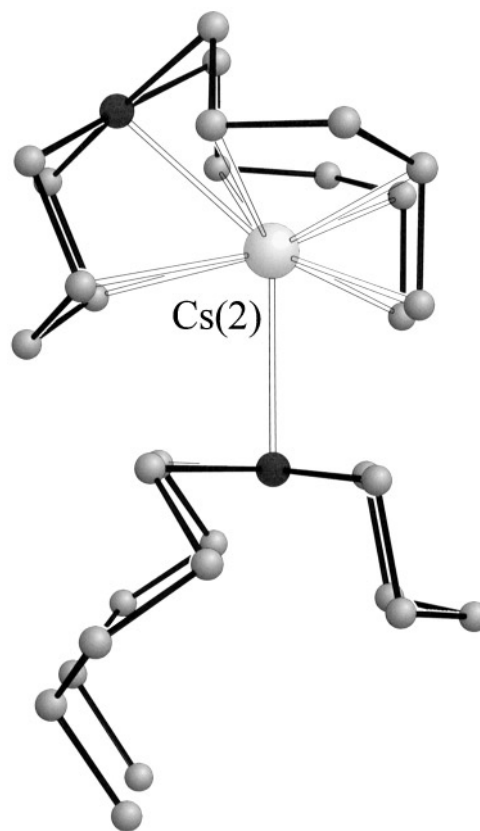


FIG. 3. Coordination sphere of $\text{Cs}(2)$ in $\text{Cs}_4\text{TeSe}_{15}$. Distances are $\text{Cs}(2)\cdots\text{Te}(1) = 3.772(4)$, $\text{Cs}(2)\cdots\text{Se}(2) = 3.886(4)$, $\text{Cs}(2)\cdots\text{Se}(5) = 4.057(3)$, $\text{Cs}(2)\cdots\text{Se}(7) = 3.818(4)$, $\text{Cs}(2)\cdots\text{Se}(8) = 3.604(4)$, and $\text{Cs}(2)\cdots\text{Te}(1') = 3.960(4)\text{ \AA}$.

tive introduction of tellurium atoms at the positions with the highest coordination number (4) in the Cs_2Te_8 structure (15). Whereas the terminal selenium atoms $\text{Se}(3)$ also extend their coordination sphere (to 3), the bridging atoms $\text{Se}(1)$ and $\text{Se}(2)$ are restricted to a coordination number with the value of their formal valency (2).

A pronounced *trans* influence is apparent for the Te–Se bonds in the distorted square-planar coordination geometry of $\text{Te}(1)$. The longer $\text{Te}(1)\cdots\text{Se}(3)$ interaction to $\text{Se}(3b)$ [$3.244(1)\text{ \AA}$] is opposite to the shortest bond $\text{Te}(1)\text{--}\text{Se}(2)$ [$2.603(1)\text{ \AA}$], the second interaction $\text{Te}(1)\cdots\text{Se}(3a)$ [$2.922(2)\text{ \AA}$] to the weaker bond $\text{Te}(1)\text{--}\text{Se}(1)$ [$2.718(2)\text{ \AA}$]. As would be predicted, the better orbital overlap for homonuclear bonds and the increased propensity of the heavier Group 16 homologue to expand its coordination sphere beyond two lead to a reduced degree of distortion for the hypervalent atoms $\text{Te}(1)$ and $\text{Te}(3)$ in Cs_2Te_8 . Thus the difference between the $\text{Te}(1)\cdots\text{Se}(3a)/\text{Te}(3a)$ and $\text{Te}(1)\cdots\text{Se}(3b)/\text{Te}(3b)$ distances is reduced from 0.322 to 0.243 \AA on going from $\text{Cs}_2\text{Te}_2\text{Se}_6$ to Cs_2Te_8 . Figure 6 depicts the stacking of individual wavelike $\frac{2}{\infty}[\text{Te}_2\text{Se}_6^{2-}]$

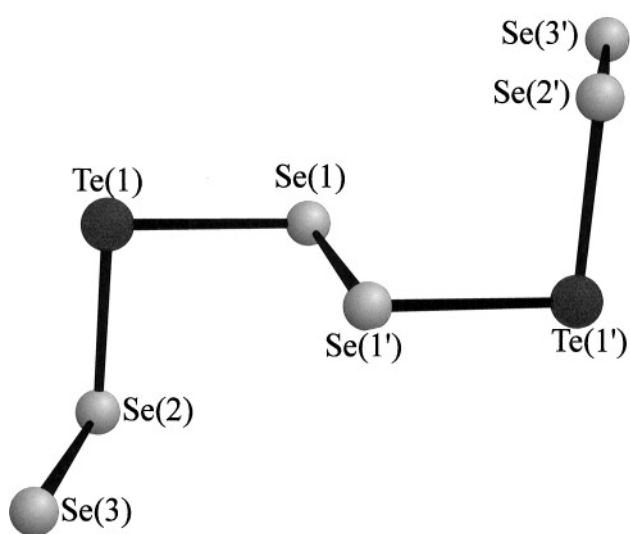


FIG. 4. The $[\text{Te}_2\text{Se}_6]^{2-}$ building units in $\text{Cs}_2\text{Te}_2\text{Se}_6$.

layers in $\text{Cs}_2\text{Te}_2\text{Se}_6$. The cesium cation Cs(1) is coordinated by two Te and eight Se atoms from a total of five symmetry-related $[\text{Te}_2\text{Se}_6]^{2-}$ chains. Distances to these nearest neighbors range from 3.639(1) [Se(1)] to 4.238(1) Å [Te(1)].

Structure of $\text{Cs}_4\text{Te}_{9.74}\text{Se}_{13.26}$

The inadequate Te content in the two crystallographically independent C_3 symmetric pyramidal $[\text{TeSe}_3]^{2-}$ anions in the unit cell of $\text{Cs}_4\text{Te}_{9.74}\text{Se}_{13.26}$ is compensated for by the presence of mixed Te/Se six-membered rings, one of which (Te_3Se_3) is ordered with a similar C_3 symmetry, whereas the second disordered neutral unit, $\text{Te}_{3.21}\text{Se}_{2.79}$, exhibits C_i symmetry. Secondary Te...Se interactions between these $\text{Te}_x\text{Se}_{6-x}$ rings and $[\text{TeSe}_3]^{2-}$ anions generate a unique rhombohedral lattice (space group $R\bar{3}$) with a long repeat unit of 44.072(9) Å in the c direction. The packing of the individual building units is depicted in Fig. 7.

Dimensions similar to those in $\text{Cs}_4\text{Te}_{9.74}\text{Se}_{13.26}$ have been observed for the pyramidal $[\text{TeSe}_3]^{2-}$ anions in Na_2TeSe_3 (2.478–2.500 Å, 100.4–102.9°) (21) and K_2TeSe_3

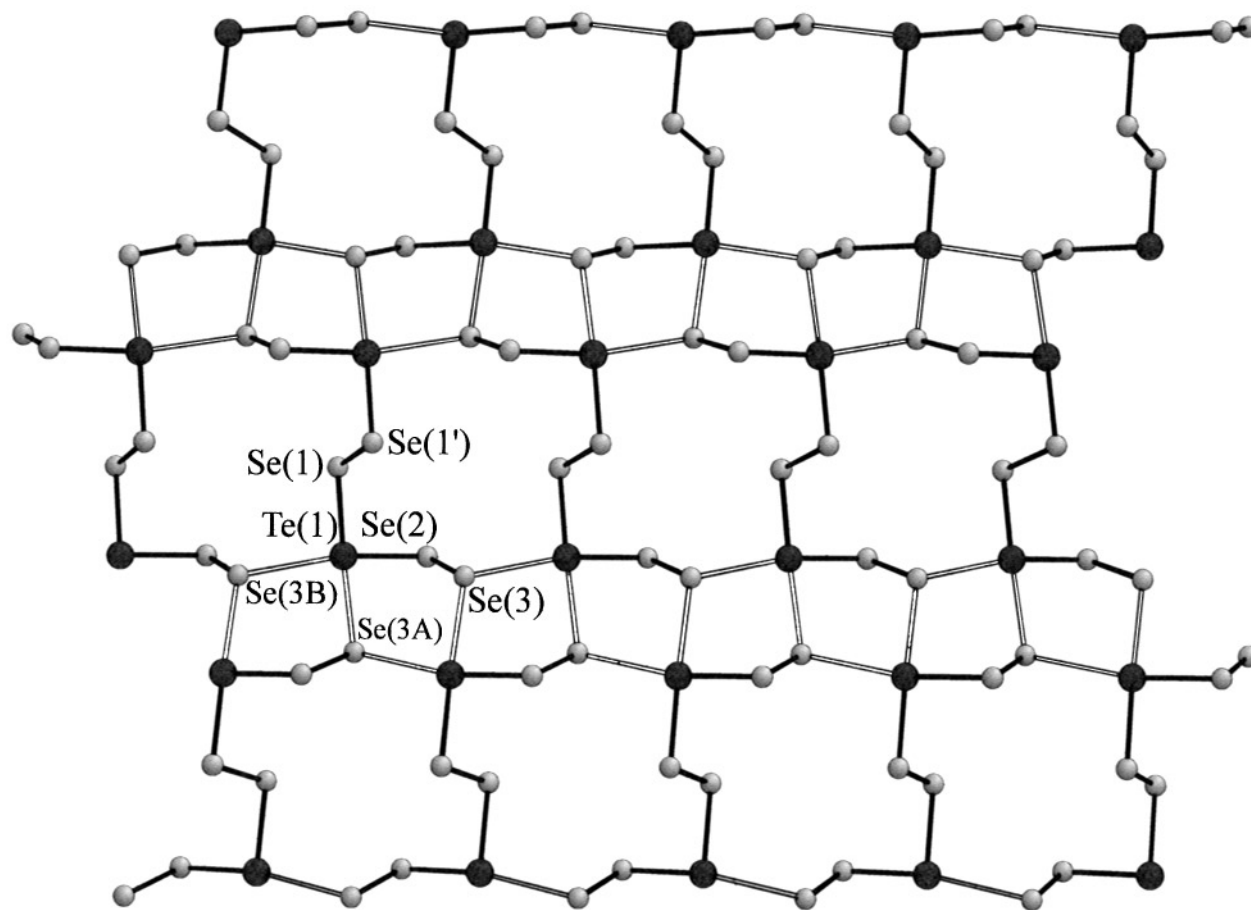


FIG. 5. Sheet structure $\frac{2}{3}[\text{Te}_2\text{Se}_6]^{2-}$ in $\text{Cs}_2\text{Te}_2\text{Se}_6$ in which individual $[\text{Te}_2\text{Se}_6]^{2-}$ units are connected through Te(1)–Se(3a) [2.922(2) Å] and Te(1)–Se(3b) [3.244(1) Å] interactions (open bonds).

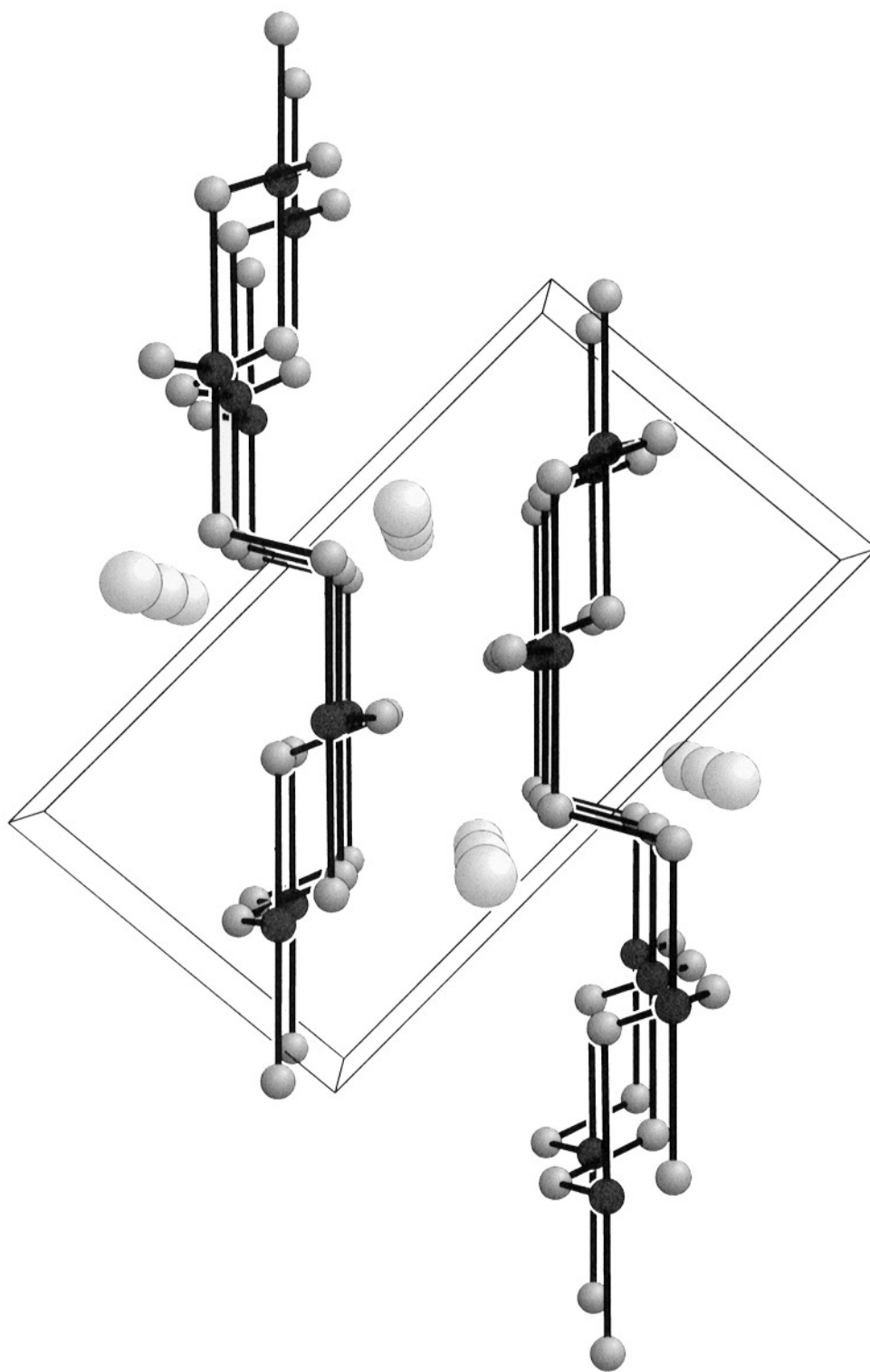


FIG. 6. Projection of the unit cell of $\text{Cs}_2\text{Te}_2\text{Se}_6$ in direction $[010]$.

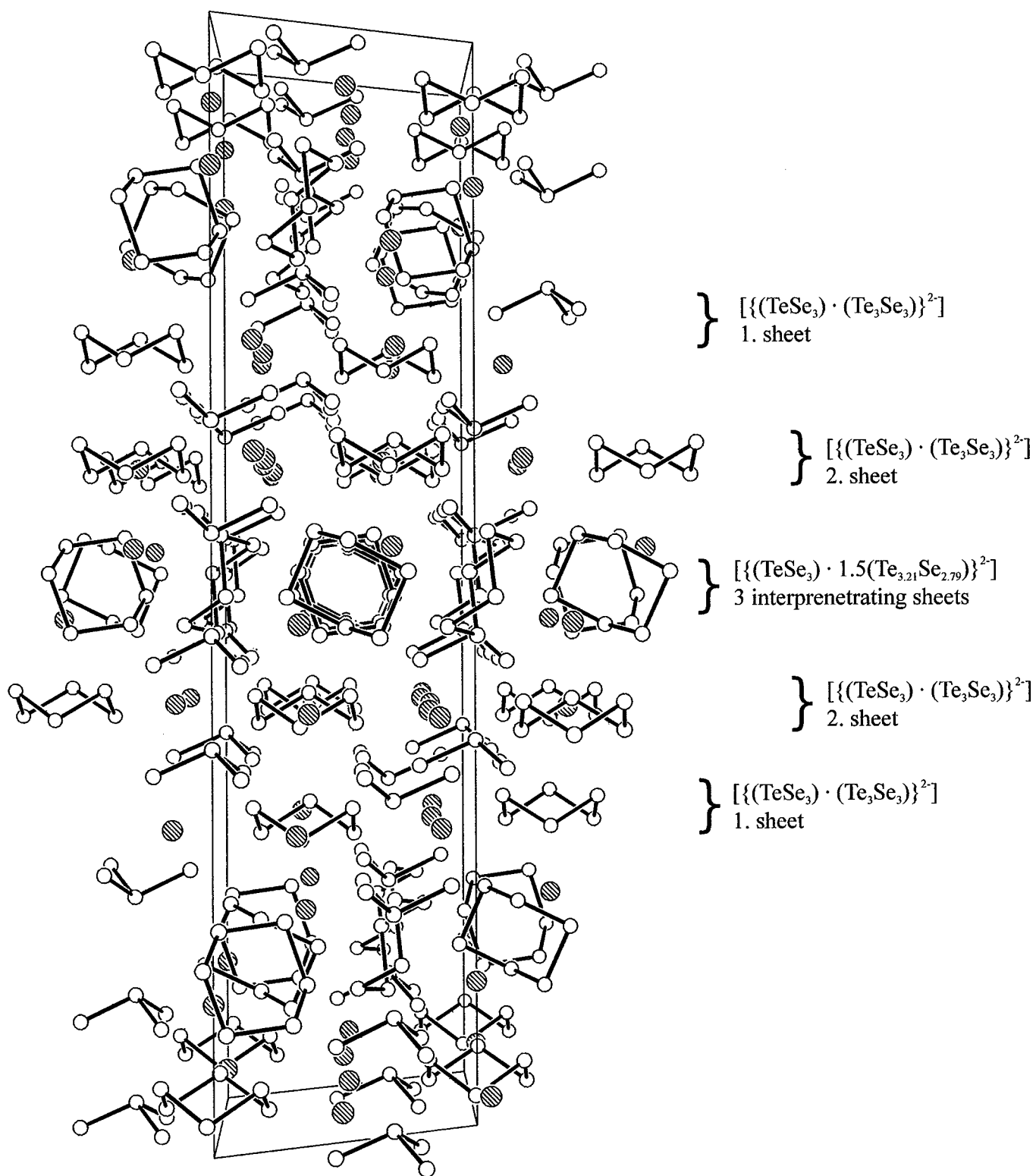


FIG. 7. Projection of the unit cell of $\text{Cs}_4\text{Te}_{9.74}\text{Se}_{13.26}$ in direction $[100]$.

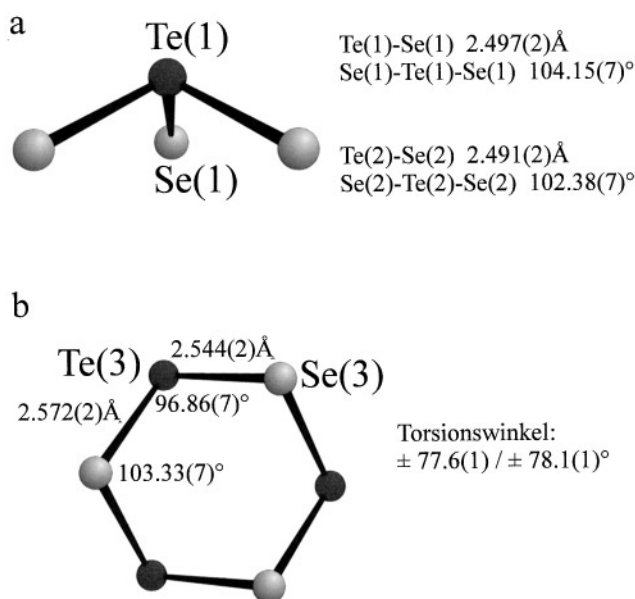


FIG. 8. Pyramidal $[\text{TeSe}_3]^{2-}$ anions $[\text{Te}(1), \text{Se}(1)]$ and ordered Te_3Se_3 $[\text{Te}(3), \text{Se}(3)]$ six-membered rings in $\text{Cs}_4\text{Te}_{9.74}\text{Se}_{13.26}$.

(2.478–2.500 Å, 101.9–105.6°) (22), which, in contrast to the present structure, are without crystallographic symmetry. The C_3 symmetric Te_3Se_3 ring [Fig. 8, $\text{Te}(3)/\text{Se}(3)$] exhibits

a chair conformation and provides the first example of an effectively isolated ordered mixed Te/Se ring system to be characterized in the solid state. Disordered $\text{Te}_x\text{Se}_{7-x}$ and $\text{Te}_x\text{Se}_{8-x}$ have been crystallized from CS_2 solution (23) and are isostructural with S_7 (24) and Se_8 (25); we have also recently reported (12) the structure of a disordered $\text{Te}_x\text{Se}_{6-x}$ ring in $\text{Cs}_3\text{AsSe}_4 \cdot 2\text{Cs}_2\text{As}_2\text{Se}_4 \cdot 6\text{Te}_4\text{Se}_2$. The $\text{Te}(3)\text{-Se}(3)$ distances in $\text{Cs}_4\text{Te}_{9.74}\text{Se}_{13.26}$ exhibit values of 2.544(2) and 2.572(2) Å, close to the sum of the covalent radii (2.54 Å) for the participating atoms. As expected, the endocyclic bond angle of 96.87(7)° at the heavier chalcogen $\text{Te}(3)$ is markedly narrower than that of 103.33(7)° for the lighter selenium atom $\text{Se}(3)$. A secondary $\text{Te}(3)\cdots\text{Se}(1)$ interaction [3.270(2) Å] between the ordered Te_3Se_3 rings and $[\text{TeSe}_3]^{2-}$ anions $[\text{Te}(1)/\text{Se}(1)]$ generates ${}_2^{\infty}[(\text{TeSe}_3^{2-}) \cdot \text{Te}_3\text{Se}_3]$ layers (Fig. 9) in which $\text{Te}(3)$ displays a distorted T-shaped coordination geometry. When a second weaker $\text{Te}(3)\cdots\text{Se}(1)$ contact of length 3.430(2) Å is considered, neighboring layers are connected into double sheets.

The symmetry-related $\text{Te}(6)$ sites in the disordered $\text{Te}_x\text{Se}_{6-x}$ rings of $\text{Cs}_4\text{Te}_{9.74}\text{S}_{13.26}$ are fully occupied by tellurium atoms and participate in analogous $\text{Te}(6)\cdots\text{Se}(2)$ interactions [3.152(2) Å] to bridging $[\text{TeSe}_3]^{2-}$ anions $[\text{Te}(2)/\text{Se}(2)]$ to afford the 6^3 net depicted in Fig. 10. Occupation of the remaining ring positions $\text{Te}/\text{Se}(4)$ and $\text{Te}/\text{Se}(5)$ by both tellurium and selenium atoms is possible. However,

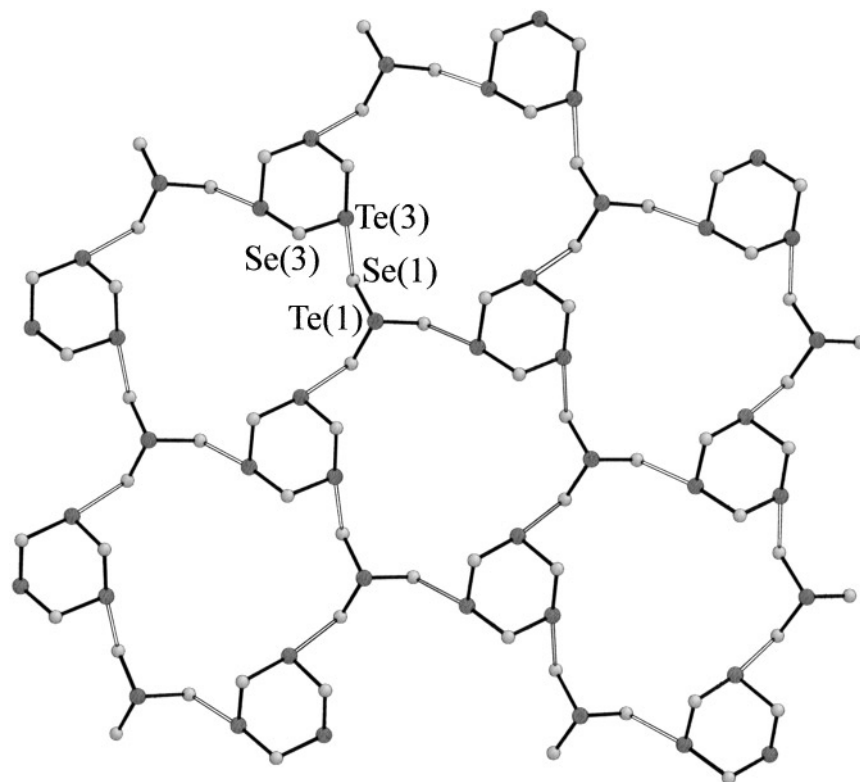


FIG. 9. ${}_2^{\infty}[(\text{TeSe}_3^{2-}) \cdot \text{Te}_3\text{Se}_3]$ sheets in $\text{Cs}_4\text{Te}_{9.74}\text{Se}_{13.26}$ containing weak $\text{Se}(1)\cdots\text{Te}(3)$ interactions of length 3.270(2) Å between pyramidal $[\text{TeSe}_3]^{2-}$ anions $[\text{Te}(1)/\text{Se}(1)]$ and ordered Te_3Se_3 six-membered rings $[\text{Te}(3)/\text{Se}(3)]$.

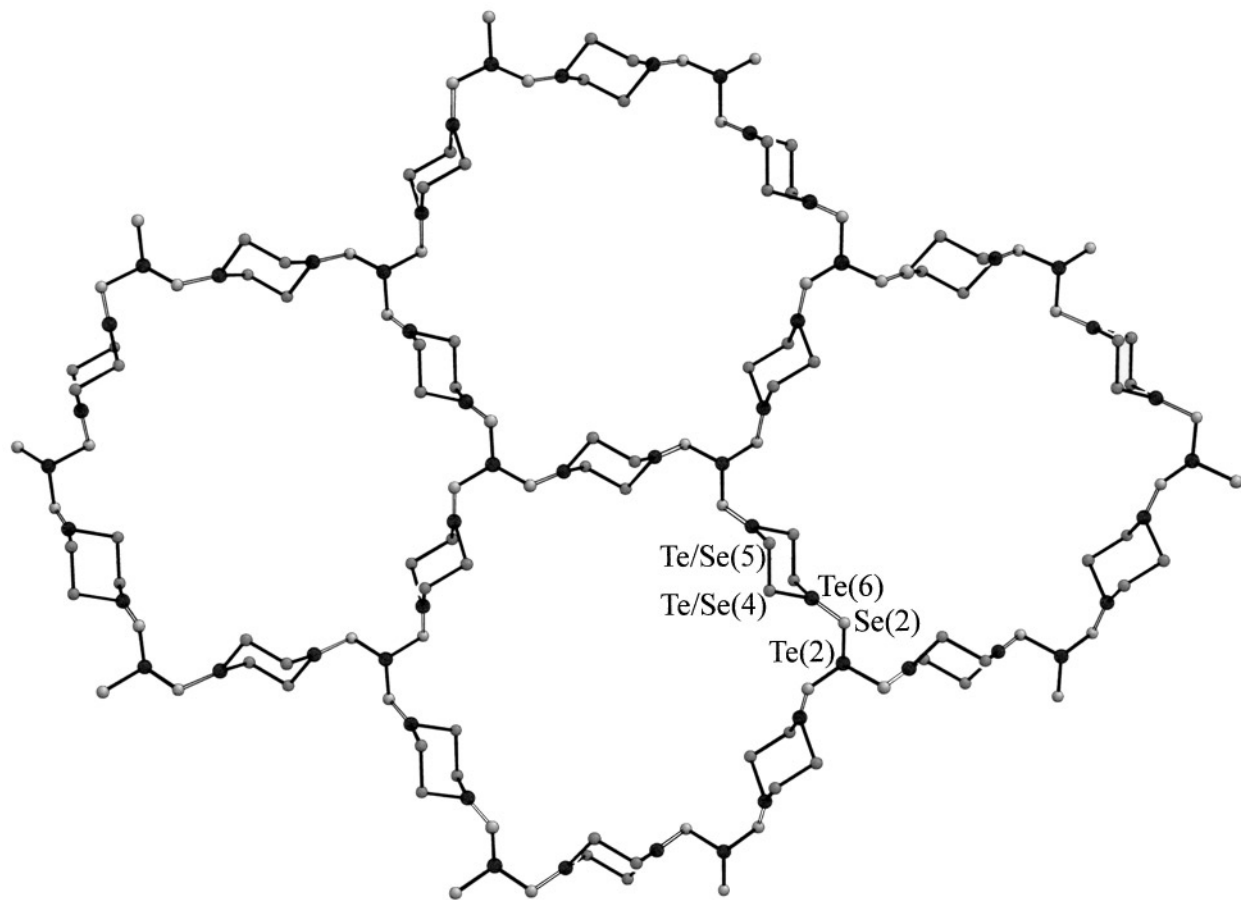


FIG. 10. $\frac{2}{\infty}[(\text{TeSe}_3^{2-}) \cdot 1.5(\text{Te}_{3.21}\text{Se}_{2.79})]$ sheets in $\text{Cs}_4\text{Te}_{9.74}\text{Se}_{13.26}$ containing weak $\text{Se}(2) \cdots \text{Te}(6)$ interactions of length $3.152(2) \text{ \AA}$ between pyramidal $[\text{TeSe}_3]^{2-}$ anions $[\text{Te}(2)/\text{Se}(2)]$ and disordered $\text{Te}_{3.21}\text{Se}_{2.79}$ six-membered rings $[\text{Te}/\text{Se}(4), \text{Te}/\text{Se}(5), \text{Te}(6)]$.

the respective refined site occupation factors of 0.19/0.81 and 0.42/0.58 suggest that six-membered Te_4Se_2 , Te_3Se_3 , and Te_2Se_4 rings will predominate in the crystal lattice. The averaged bond distances of 2.51 \AA $[\text{Te}/\text{Se}(4) - \text{Te}/\text{Se}(5)]$, 2.72 \AA $[\text{Te}/\text{Se}(5) - \text{Te}(6)]$, and 2.60 \AA $[\text{Te}/\text{Se}(4) - \text{Te}(6)]$ are in accordance with this proposal, as are the bond angles of 104.6° $[\text{Te}/\text{Se}(4)]$, 99.8° $[\text{Te}/\text{Se}(5)]$, and 96.1° $[\text{Te}(6)]$ for the disordered ring system. As demonstrated in Fig. 11, neighboring 6^3 nets are interpenetrating with a closest contact $\text{Te}/\text{Se}(5) \cdots \text{Se}(2)$ of $3.254(2) \text{ \AA}$. One of the three individual nets is highlighted with the help of a dotted hexagon. TeSe_3 units of the other two interpenetrating layers are positioned on the C_3 axis running through the middle of this hexagon.

CONCLUSION

The crystallization of polychalcogenides from superheated methanol solutions in the temperature range $100\text{--}200^\circ\text{C}$ favors the formation of both E_x^{2-} chains

($E = \text{Se}, \text{Te}$) and E_n rings. Our present work provides novel examples of ordered mixed Te/Se chains ($[\text{Te}_2\text{Se}_6]^{2-}$ in $\text{Cs}_2\text{Te}_2\text{Se}_6$) and rings (TeSe_5 in $\text{Cs}_4\text{TeSe}_{15}$, Te_3Se_3 in $\text{Cs}_4\text{Te}_{9.74}\text{Se}_{13.26}$). Longer $\text{Te} \cdots \text{Se}$ interactions between individual chains and rings generate polymeric anionic sheets in $\text{Cs}_2\text{Te}_2\text{Se}_6$ and $\text{Cs}_4\text{Te}_{9.74}\text{Se}_{13.26}$. The heavier Te atoms preferentially adopt sites with higher coordination numbers (3 or 4) in these compounds. The mechanism for the formation of these products is not yet clear. We were unable to isolate Sb - or Bi -containing anions and, in the case of Sb , powder diffraction patterns only provide further lines belonging to the reactant Sb_2Te_3 . An alternative method which also uses Group 15 tellurides as reactants is given by the novel electrochemical synthesis method recently developed by Haushalter *et al.* It allows the generation of As - or Sb -containing anions at room temperature by employing the cathodic dissolution of different alloy electrodes in an solution containing a quaternary ammonium salt as the cation source. Product formation is strongly dependent on the size of this ammonium salt. For example, the dissolution

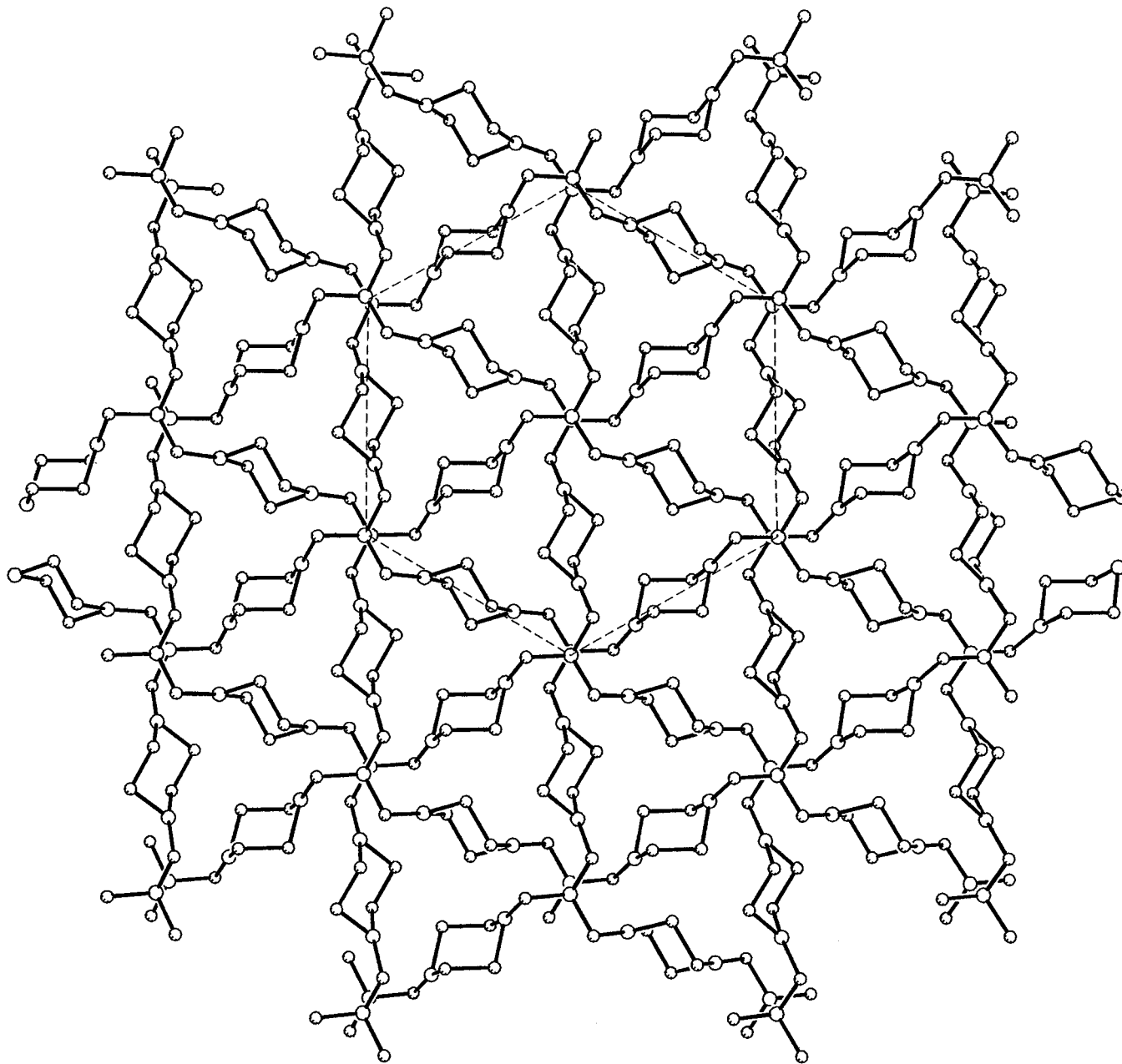


FIG. 11. The three interpenetrating $\frac{2}{3}[(\text{TeSe}_3^{2-}) \cdot 1.5(\text{Te}_{3.21}\text{Se}_{2.79})]$ sheets in $\text{Cs}_4\text{Te}_{9.74}\text{Se}_{13.26}$, one of which is highlighted with the help of a dotted hexagon.

of an Sb_2Te_3 cathode in an en solution containing $(\text{R}_4\text{N})\text{I}$ ($\text{R} = \text{Me}, \text{Et}, n\text{-Pr}$) yields respectively $(\text{Me}_4\text{N})_4[\text{Sb}_2\text{Te}_5]$, $(\text{Et}_4\text{N})_4[\text{Sb}_2\text{Te}_5]/(\text{Et}_4\text{N})_4[\text{Sb}_6\text{Te}_9] \cdot 0.5\text{en}$, and $(\text{Pr}_4\text{N})_4[\text{Sb}_4\text{Te}_4]/(\text{Pr}_4\text{N})_3[\text{Sb}_9\text{Te}_6]$ (26). If the electrode material is changed to NiSb_2Te_6 , or SbSn_2Te_6 , an en solution containing $(\text{Bu}_4\text{N})\text{I}$ generates the compound $(\text{Bu}_4\text{N})_3[\text{SbTe}_2(\text{Te}_2)]$ (27). Ni or Sn is not found in the products. Finally, if the Te/element ratio is further increased in the electrode mater-

ial, only Te-containing products are obtained, as shown by the dissolution of an SbTe_{10} alloy electrode in a solution of $(\text{Et}_4\text{N})\text{I}$ in en (28).

In the case of our methanolothermal route, the product formation appears to be more dependent on the solubility of the used binary Group 15 tellurides. As_2Te_3 is, in comparison to Sb_2Te_3 or Bi_2Te_3 , rather soluble in MeOH itself and so it may be used to generate As-containing products. Reac-

tions with this telluride provide Cs₄As₂Te₆ (29) and, in the case of additional Se, novel quaternary compounds (30).

The findings reported here suggest that the selective methanolothermal incorporation of tellurium atoms should also be possible for other polychalcogenides and chalcogenidometalates ($E = S, Se$) at such chalcogen positions that readily allow an increase in coordination number through secondary interactions with neighboring building units.

REFERENCES

- (a) A. Stein, S. W. Keller, and T. E. Mallouk, *Science* **259**, 1558 (1993); (b) J. Gopalakrishnan, *Chem. Mater.* **7**, 1265 (1995).
- (a) M. G. Kanatzidis, *Chem. Mater.* **2**, 353 (1990); (b) Y. Park, J.-H. Liao, K.-W. Kim, and M. G. Kanatzidis, in "Inorganic and Organometallic Oligomers and Polymers" (J. F. Harrod and R. M. Laine, Eds.), p. 263. Kluwer Academic, Dordrecht, 1991; (c) M. G. Kanatzidis, *Phosphorus, Sulfur, Silicon Relat. Elem.* **93**, 159 (1994); (d) M. G. Kanatzidis and C. Sutorik, *Prog. Inorg. Chem.* **43**, 151 (1995); (e) M. A. Ansari and J. A. Ibers, *Coord. Chem. Rev.* **100**, 223 (1990).
- W. S. Sheldrick and M. Wachhold, *Angew. Chem. Int. Ed. Engl.* **36**, 206 (1997).
- (a) R. H. Arnston, F. W. Dickson, and G. Tunell, *Science* **128**, 716 (1958); (b) *Am. J. Sci.* **258**, 574 (1960); (c) W. F. Giggensbach, *Inorg. Chem.* **11**, 1201 (1972); (d) *ibid.*, **13**, 1724 (1974); (e) L. Henriksen, in "Proceedings of the 4th International Conference on the Organic Chemistry of Selenium and Tellurium" (F. J. Berry and W. R. McWhinnie, Eds.), p. 242. The University of Aston, Birmingham, 1983.
- W. S. Sheldrick and H. G. Braunbeck, *Z. Naturforsch. B* **44**, 1397 (1989).
- (a) P. Böttcher, *J. Less-Common Met.* **70**, 263 (1980); (b) P. Böttcher and U. Kretschmann, *Z. Anorg. Allg. Chem.* **491**, 39 (1982).
- W. S. Sheldrick and B. Schaaf, *Z. Naturforsch., B* **49**, 993 (1994).
- W. S. Sheldrick and M. Wachhold, *J. Chem. Soc., Chem. Commun.* 607 (1996).
- W. S. Sheldrick and M. Wachhold, *Angew. Chem., Int. Ed. Engl.* **34**, 450 (1995).
- (a) Q. Liu, N. Goldberg, and R. Hoffmann, *Chem. Eur. J.* **2**, 390 (1996); (b) S. Jobic, W. S. Sheldrick, E. Canadell, and R. Brec, *Bull. Soc. Chim. Fr.* **133**, 221 (1996); (c) W. S. Sheldrick, M. Wachhold, S. Jobic, R. Brec, S. Alvarez, and E. Canadell, *Adv. Mater.* **9**, 669 (1997); (d) S. Lee and B. J. Foran, *J. Am. Chem. Soc.* **118**, 9139 (1996); (e) R. Hoffmann, *Am. J. Sci.* **84**, 327 (1996).
- M. Wachhold and W. S. Sheldrick, *Z. Naturforsch., B* **51**, 32 (1996).
- M. Wachhold and W. S. Sheldrick, *Z. Naturforsch., B* **52**, 169 (1997).
- P. Böttcher and U. Kretschmann, *J. Less-Common Met.* **95**, 81 (1983).
- U. Kretschmann and P. Böttcher, *Z. Naturforsch., B* **40**, 895 (1985).
- P. Böttcher and U. Kretschmann, *Z. Anorg. Allg. Chem.* **523**, 145 (1985).
- G. M. Sheldrick, "SHELXS-86, Program for Crystal Structure Solution," Göttingen, 1986.
- G. M. Sheldrick, "SHELXL-93, Program for Crystal Structure Refinement," Göttingen, 1993.
- P. Böttcher, *Z. Kristallogr.* **150**, 65 (1979).
- G. Kräuter, K. Dehnicke, and D. Fenske, *Chem.-Zt.* **114**, 7 (1990).
- R. Zagler and B. Eisenmann, *Z. Naturforsch., B* **46**, 593 (1991).
- R. Zagler and B. Eisenmann, *Z. Kristallogr.* **183**, 193 (1988).
- B. Eisenmann and R. Zagler, *Z. Kristallogr.* **185**, 473 (1988).
- (a) K. Nagata, H. Hayashi, and Y. Miyamoto, *Fukuoka Univ. Sci. Rep.* **18**, 23 (1988); (b) K. Nagata, H. Hayashi, and Y. Miyamoto, *Fukuoka Univ. Sci. Rep.* **18**, 35 (1988).
- R. Steudel, J. Steidel, J. Pickardt, F. Schuster, and F. Reinhardt, *Z. Naturforsch., B* **35**, 1378 (1980).
- P. Cherin and P. Unger, *Acta Crystallogr., B* **28**, 313 (1972).
- (a) C. J. Warren, D. M. Ho, R. C. Haushalter, and A. B. Bocarsly, *Angew. Chem.* **105**, 1684 (1993); *Angew. Chem., Int. Ed. Engl.* **32**, 1646 (1993); (b) C. J. Warren, S. S. Dhingra, D. M. Ho, R. C. Haushalter, and A. B. Bocarsly, *Inorg. Chem.* **33**, 2709 (1994).
- J. L. Shreeve-Keyer and R. C. Haushalter, *Polyhedron* **15**, 1215 (1996).
- (a) C. J. Warren, R. C. Haushalter, and A. B. Bocarsly, *J. Alloys Compd.* **233**, 23 (1996); (b) C. J. Warren, R. C. Haushalter, and A. B. Bocarsly, *J. Alloys Compd.* **229**, 175 (1995).
- M. Wachhold and W. S. Sheldrick, *Z. Naturforsch., B* **51**, 1235 (1996).
- W. S. Sheldrick and M. Wachhold. [manuscript in preparation].