Sn_9^{4-} Zintl Ions as Reactive Precursor for Neat Solids: Syntheses and Crystal Structures of $Rb_4[SnTe_4]$, $K_xCs_{4-x}[SnTe_4]$, and $K_xCs_{10-x}[Sn_4Te_{12}]$

Jian-Qiang Wang, Viktor Hlukhyy, and Thomas F. Fässler

Department Chemie, Technische Universität München, Lichtenbergstraße 4, 85747 Garching, Germany

Reprint requests to Prof. Dr. Thomas F. Fässler. E-mail: thomas.faessler@lrz.tum.de

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

The reactions of Zintl ions Sn_9^{4-} formed in ethylenediamine solutions of $K_2Cs_2Sn_9$ and Rb_4Sn_9 with elemental tellurium have been investigated. Addition of elemental tellurium to the filtrates of these solutions leads – depending on the reaction conditions – to four different products: Compounds $K_{0.36(1)}Cs_{3.64(1)}[SnTe_4]$ (**1**) and $Rb_4[SnTe_4]$ (**2**) contain the tetrahedral anion $[SnTe_4]^{4-}$, and $Cs_4[Sn_2Te_7]$ (**3**) features the anion $[Te_2Sn(\mu\text{-}Te)(\mu\text{-}Te_2)SnTe_2]^{4-}$, whereas a novel Zintl anion $[Sn_4Te_{12}]^{10-}$ is present in compound $K_{0.44(1)}Cs_{9.56(1)}[Sn_4Te_{12}]$ (**4**). Compounds **1**, **2** and **4** have been structurally characterized by single-crystal X-ray diffraction.

Key words: Zintl Ions, Crystal Structure, Tellurium

Introduction

In the past decades, metal chalcogenides have extensively been studied [1]. Among these main group chalcogenidometalates such as $[Ge_4S_{10}]^{4-}$ [2], $[SnSe_4]^{4-}$ [3], or $[Sn_2Se_6]^{4-}$ [4] are of particular interest because of their structural diversity and their apparent technological potential as precursors to some multifunctional materials [5]. In this context the compounds containing $[Sn_xTe_y]^{q-}$ ions have been obtained mainly by three methods [6]. In the first method elemental tin and tellurium are fused together at high temperature [7]. However, most of the so obtained high-temperature phases contain only relatively simple anionic units, and the formation of larger aggregates like chains or rings have not been observed under these conditions. The second method is the hydro- (or solvo-) thermal synthesis [8]. In this case smaller units assemble to larger anionic aggregates of various structures. The third, less explored method is based on reactions in solution in which different simple starting materials are employed to react in appropriate solvents under mild controllable conditions. This route offers a broad range of variations which as yet have not been explored comprehensively [9].

Thus, we became interested in solution reactions of $[E_9]^{4-}$ Zintl ions (E = Ge, Sn, and Pb) [10] and showed in a previous study that the reaction of K_4Sn_9 with elemental tellurium in solution led to the formation of the anion $[Te_2Sn(\mu\text{-}Te)_2SnTe_2]^{4-}$ and – after the addition of Me_3NO – to $[Sn(\mu\text{-}Te)_3Sn]^{2-}$ [11]. A more general method to obtain Zintl ions from solutions is the use of a sequestering agent for the countercation, such as 2,2,2–crypt [12] or 18–crown–6 [10a]. The presence of a sequestering agent very often facilitates the crystallization of the Zintl ion-containing compounds [13], but in order to obtain neat Zintl phases the presence of sequestering agents in the solution should be avoided.

Herein, we report on the reactions of Group 14 Zintl ions with elemental tellurium in the absence of cation-sequestering agents, and describe the structures of the products.

Results and Discussion

The reactions were carried out in ethylenediamine solutions of $K_2Cs_2Sn_9$ and Rb_4Sn_9 both of which are known to contain the Zintl anion $[Sn_9]^{4-}$ with a ten-fold excess of elemental tellurium in the absence of any sequestering agents. Interestingly, a change of the

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Table 1. Crystallographic data and structural refinement details of **1**, **2**, and **4**.

Compound	**1**	**2**	**4**
Empirical formula	$K_{0.36(1)}Cs_{3.64(1)}[SnTe_4]$	$Rb_{4.00(1)}[SnTe_4]$	$K_{0.44(1)}Cs_{9.56(1)}[Sn_4Te_{12}]$
Formula weight	1129.07	970.97	3294.16
Crystal system	hexagonal	hexagonal	trigonal
Space group	*P6/m*	*P6/m*	$P\bar{3}1c$
Z	12	12	4
a, Å	23.3138(4)	22.6040(4)	17.6320(6)
b, Å	23.3138(4)	22.6040(4)	17.6320(6)
c, Å	12.0927(3)	11.8155(4)	23.472(1)
V, Å^3	5692.2(2)	5228.2(2)	6319.6(4)
T, K	153	153	153
ρ_{calcd}, g cm^{-3}	3.95	3.70	3.46
μ (MoK_α), mm^{-1}	14.3	19.1	12.5
Refls. observed	22915	20550	38914
Data / parameters	3497 / 102	3244 / 101	3719 / 85
Goodness of fit	0.997	0.948	0.847
R_1 [$I \geq 2\sigma(I)$]	0.0415	0.0563	0.0413
wR_2 [$I \geq 2\sigma(I)$]	0.0990	0.1155	0.1026
R_1 (all data)	0.0726	0.1217	0.0862
wR_2 (all data)	0.1238	0.1410	0.1083
Largest diff. peak / hole, e Å^3	2.97 / −2.18	3.18 / −3.61	2.88 / −2.14

reaction conditions led to the formation of different products. When the ethylenediamine solution of the Zintl phase $K_2Cs_2Sn_9$ was mixed with elemental tellurium at r. t. and under vigorous stirring, it reacted quickly, and the color of the reaction mixture changed from dark-red to orange within half an hour. After filtration and layering of the filtrate with toluene large red block-shaped crystals of $K_{0.36(1)}Cs_{3.64(1)}[SnTe_4]$ (**1**) separated, accompanied by a small amount of orange needles identified as $Cs_4[Sn_2Te_7]$ (**3**), which was obtained in a high-temperature synthesis and structurally characterized by Schäfer and coworkers already in 1985 [15]. Under the same conditions Rb_4Sn_9 and Te reacted exclusively to $Rb_4[SnTe_4]$ (**2**). Compound **2** was obtained in the filtrate as red crystals after one week. However, when an ethylenediamine solution of $K_2Cs_2Sn_9$ was carefully added to tellurium powder without stirring, and the mixture was then kept undisturbed for 12 hours, red crystal of $K_{0.44(1)}Cs_{9.56(1)}[Sn_4Te_{12}]$ (**4**) appeared in the filtrate after one week.The structures of compounds **1**, **2** and **4** have been determined by single-crystal X-ray diffraction (Table 1).

The $[SnTe_4]^{4-}$ anion present in compounds **1** and **2** has been found and structurally characterized by X-ray crystallography before in combination with a large number of different counter cations [14]. In compound **1** it is counterbalanced by K^+/Cs^+, Cs^+ cations and has the expected structure of an isolated, almost perfect tetrahedron shown in Fig. 1, with Sn-Te bond lengths and Te-Sn-Te bond angles given in the Figure caption similar to those reported previously [14]. The same holds for the $[SnTe_4]^{4-}$ anion in compound **2**.

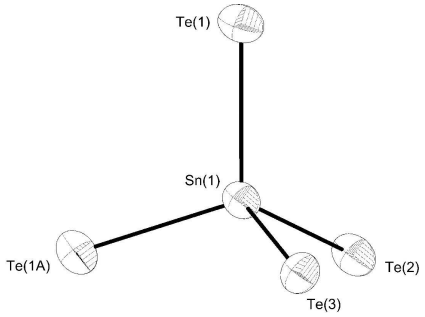


Fig. 1. Structure of the $[SnTe_4]^{4-}$ anion in compound $K_{0.36(1)}Cs_{3.64(1)}[SnTe_4]$ (**1**). Displacement ellipsoids are drawn at 50 % probality. Selected bond lengths (Å) and angles (deg): Sn(1)-Te(1) 2.741(1), Sn(1)-Te(2) 2.719(2), Sn(1)-Te(3) 2.744(2); Te(1)-Sn(1)-Te(2) 109.59(5), Te(1)-Sn(1)-Te(3) 112.54(5), Te(2)-Sn(1)-Te(3) 104.85(7), Te(1A)-Sn(1)-Te(1) 107.69(7), Te(1A)-Sn(1)-Te(2) 109.59(5), Te(1A)-Sn(1)-Te(3) 112.53(5).

Compound $K_{0.44(1)}Cs_{9.56(1)}[Sn_4Te_{12}]$ (**4**) represents a novel Zintl phase. Its crystal structure is composed of K^+/Cs^+, Cs^+ cations and the unprecedented anion $[Sn_4Te_{12}]^{10-}$. This polyanion consists of one pyramidal $SnTe_3$ unit [Sn(1)] which is connected to three $SnTe_4$ tetrahedra [Sn(2)] *via* its Te atoms (Fig. 2). The Sn(1)–Te(4) distance in the pyramidal unit is 2.897(1) Å. The Sn(2)–Te bond lengths in the tetrahedra are shorter and range from 2.703(1) to 2.769(1) Å, which can be rationalized by the higher formal oxidation state ("valence") of +4 of Sn(2) and the lower

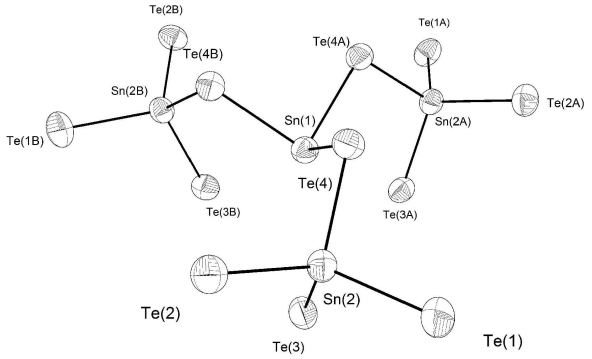


Fig. 2. Structure of the $[Sn_4Te_{12}]^{10-}$ anion in compound $K_{0.44(1)}Cs_{9.56(1)}[Sn_4Te_{12}]$ (**4**). Displacement ellipsoids are drawn at 50 % probality. Selected bond lengths (Å) and angles (deg): Sn(1)-Te(4) 2.897(1), Sn(2)-Te(1) 2.723(2), Sn(2)-Te(2) 2.703(1), Sn(2)-Te(3) 2.710(2), Sn(2)-Te(4) 2.769(1); Te(4)-Sn(1)-Te(4A) 89.67(5), Sn(2)-Te(4)-Sn(1) 98.63(4), Te(1)-Sn(2)-Te(2) 113.98(5), Te(1)-Sn(2)-Te(4) 104.06(5), Te(1)-Sn(2)-Te(3) 111.00(5), Te(2)-Sn(2)-Te(3) 111.34(5), Te(2)-Sn(2)-Te(4) 108.59(5), Te(3)-Sn(2)-Te(4) 107.37(5).

formal oxidation state of +2 of Sn(1). The average Sn(2)-$Te_{terminal}$ bond length of 2.713(2) Å is close to the average Sn-Te distance in the isolated tetrahedral anions $[SnTe_4]^{4-}$ (2.732 Å) [14], and longer than in $[Sn_2Te_7]^{4-}$ (2.683(3) Å) [15]. Furthermore, the Sn(2)–$Te_{terminal}$ distances are shorter than the sum of the Te (covalent) and the Sn(IV) radii (1.37 and 1.40 Å, respectively) of 2.77 Å [16].

As already mentioned above, many tin-telluride Zintl phases – including now also compounds **1** and **2** – contain isolated tetrahedral $SnTe_4$ building blocks [14]. The anion of $Cs_4Sn_2Te_7$ forms a dimer of corner-sharing tetrahedra [15], and in $[(en)H]_4Sn_2Te_6$ [17], $(Me_4N)_4Sn_2Te_6$ [18], $(Et_4N)_4Sn_2Te_6$ [19], and $[M(en)_3]Sn_2Te_6$ (M = Zn, Mn) [20] the dimeric anions consist of edge-sharing tetrahedra. Furthermore, various types of anionic (1D) chains with a Sn/Te backbone have been found, *e. g.* in Ba_2SnTe_5 [21], where vertex-sharing $SnTe_4$ tetrahedra build up the chains or in $K_2HgSnTe_4$ [22] and $Cs_2MnSnTe_4$ [23], which contain edge-sharing $SnTe_4$ tetrahedra. Chains of $SnTe_4$ tetrahedra which are linked *via* Te-Te bonds occur in Cs_2SnTe_4 [24] and in K_2SnTe_5 [25]. In Tl_2SnTe_5 $SnTe_4$ tetrahedra are interconnected with planar Te_5 units [26], whereas $K_2Ag_2SnTe_4$ contains vertex- and edge-sharing $SnTe_4$ and $AgTe_4$ tetrahedra that form a three-dimensional network [27]. The anion of compound **4** represents a novel oligomer based on $SnTe_4$ tetrahedral building blocks in this series of compounds.

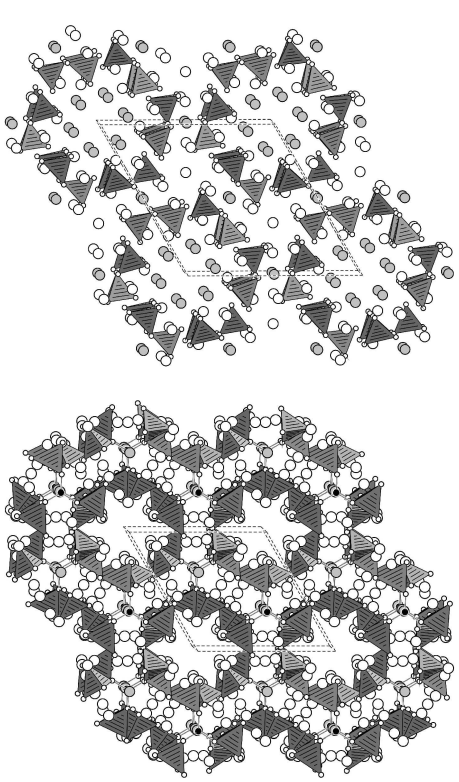
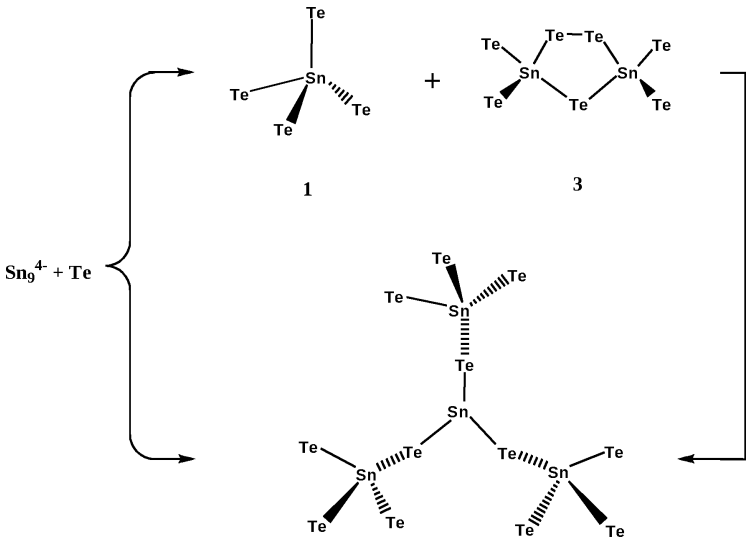


Fig. 3. The view of the crystal structures of (a) $K_{0.36(1)}Cs_{3.64(1)}[SnTe_4]$ (**1**) and (b) $K_{0.44(1)}Cs_{9.56(1)}$-$[Sn_4Te_{12}]$ (**4**) along the *c* axis, underlining the large zeolite-like channels. $[SnTe_4]^{4-}$ and $[Sn_4Te_{12}]^{10-}$ anions are emphasized as polyhedral building units. Cs, Cs/K, Te, and Sn atoms are drawn as large white, grey, small white, and black circles, respectively.

A closer look at the ion packing in $K_{0.36(1)}Cs_{3.64(1)}$-$[SnTe_4]$ (**1**), $Rb_{4.00(1)}SnTe_4$ (**2**), and $K_{0.44(1)}Cs_{9.56(1)}$-$[Sn_4Te_{12}]$ (**4**) reveals the presence of channels along the *c* directions of the unit cells, as shown in Fig. 3 for **1** and **4**. In the case of **1** and **2** the volume per formula unit of 474.4 and 435.7 $Å^3$ (153 K), respectively, compares well with those of $[Rb_4(H_2O)_2][SnTe_4]$ (430.1 $Å^3$, 203 K) and $[Rb_4(H_2O)_{0.67}(en)_{0.33}][SnTe_4]$ (445.8 $Å^3$, 203 K) [14b]. The slightly larger volume of $Rb_4[SnTe_4]$ (**2**) suggests inclusion of small amounts of solvent molecules, but to a lesser extent than in $[Rb_4(H_2O)_{0.67}(en)_{0.33}][SnTe_4]$. Similarly, we cannot fully exclude inclusion of solvent molecules in the channels of compound **4**; however, we did not find any distinct maxima of the residual electron density.

The presence of the oligomeric anion in compound **4** together with the observed existence of three different kinds of Sn-Te compounds in the reactions as



Scheme 1.

summarized in Scheme 1 may provide insight into the mechanism of the oligomerization process of the Sn/Te species. At a first step of the reaction, Te atoms may insert into the Sn–Sn bonds of the Sn_9^{4-} cluster. Then cluster opening and defragmentation may occur by further reaction with Te. As one of the larger fragments of this process the anion of compound **4** is formed which still contains four Sn atoms. Further reaction with Te finally leads to the monomeric unit $[SnTe_4]^{4-}$. It is reasonable to assume that the polymerization of Sn-Te clusters can be influenced by the solvent and the reaction conditions. Studies in this direction are currently in progress.

Experimental Section

All reactions and manipulations were performed under an argon atmosphere using a glove box or Schlenk line. Ethylenediamine (Merck, 99 %) was dried over CaH_2 and freshly distilled and degassed prior to use. The phases of formal compositions $K_2Cs_2Sn_9$ and Rb_4Sn_9 were synthesized from stoichiometric (2 : 2 : 9 for $K_2Cs_2Sn_9$ and 4 : 9 for Rb_4Sn_9) mixtures of the elements (K: Merck, 99 %; Cs: Aldrich, 99.9 %; Sn: Merck, 99.9 %) heated at 740 °C for 20 h in a sealed stainless-steel container jacketed with an argon-filled fused-silica tube. The Te powder (ABCR, 99.9 %) was used as received after careful drying under vacuum.

Reaction of $K_2Cs_2Sn_9$ with elemental tellurium

(a) $K_2Cs_2Sn_9$ (150 mg, 0.11 mmol), was dissolved in ethylenediamine (1 mL). The solution was stirred for 0.5 h, and tellurium powder (127 mg, 1 mmol) was added to the dark-red solution. The reaction mixture was stirred for 1 h during which time its color changed to orange. After filtration, the solution was layered with toluene and left undisturbed for one week. Large block-shaped red crystals of **1** and a small amount of orange needles of **3** appeared at the bottom of the flask. EDX analyses showed a ratio K : Cs : Sn : Te of 1 : 7 : 2 : 8 for **1**, and a ratio Cs : Sn : Te of 4 : 2 : 7 for **3**.

(b) $K_2Cs_2Sn_9$ (150 mg, 0.11 mmol), was dissolved in ethylenediamine (1 mL). The solution was stirred for 0.5 h, and transferred to a flask which contained solid tellurium powder (127 mg, 1 mmol) without stirring. The reaction mixture was left undisturbed for 12 h, then it was filtered, and the filtrate layered with toluene. Red crystals of **4** appeared within one week. The EDX analysis showed a ratio K : Cs : Sn : Te of 1 : 9 : 4 : 12 for **4**.

Reaction of Rb_4Sn_9 with elemental tellurium

Rb_4Sn_9 (150 mg, 0.11 mmol), was dissolved in ethylenediamine (1 mL). The solution was stirred for 0.5 h, and tellurium powder (127 mg, 1 mmol) was added to the dark-red solution. The reaction mixture was stirred for 1 h during which time its color changed to orange. After filtration, the solution was layered with toluene and left undisturbed. Red crystals of **2** were obtained within one week. The EDX analysis showed a ratio Rb : Sn : Te of 4 : 1 : 4 for **2**.

X-Ray diffraction and structure refinement

Single-crystal X-ray diffraction data were collected at 153 K on an Oxford Xcalibur3 diffractometer with a CCD area detector (graphite-monochromated MoK_α radiation,

crystals were protected by perfluoropolyalkyether oil). The structures were solved by Direct Methods and refined on F^2 using the SHELXTL V6.1 package [28] with anisotropic atomic displacement parameters for all atoms. The occupancy parameters were refined in separate series of least-squares cycles in order to check for defects or possible mixed occupancies. This procedure revealed defects on the Rb6 and Rb7 positions in the structure of **2** with reasonable displacement parameters and lower *R*-values for s. o. f. values of *ca.* 87 at-% and 79 at-%, respectively, corresponding to a composition of "$Rb_{4.00(1)}TeSn_4$" which is in accord with the ideal formula of Rb_4TeSn_4. Cs6 and Cs7 positions of isostructural **1** are occupied by 77 at-% and 90 at-%, respectively. Besides the defects, two mixed Cs/K positions were revealed, leading to the final composition $K_{0.36(1)}Cs_{3.64(1)}[SnTe_4]$ for **1**. In structure **4**, a large ellipsoid occurs for Cs5 in position 6*h*, therefore it was refined by a split model at position 12*i* with an atom site population of 50 %. On position 4*f* a mixed occupancy with 56 at-% Cs and 44 at-% K was observed leading to the composition $K_{0.44(1)}Cs_{9.56(1)}[Sn_4Te_{12}]$. Contributions of small amounts of disordered solvate molecules in the channels depicted in Fig. 3 to the structure factors were taken care of by the SQUEEZE option of PLATON [29]. All relevant crystallographic data for the data collections and evaluations are listed in Table 1.

Further details on the structure refinement may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No's. CSD–421132 ($K_{0.36(1)}Cs_{3.64(1)}[SnTe_4]$), CSD–421133 ($Rb_4[SnTe_4]$), and CSD–421134 ($K_{0.44(1)}Cs_{9.56(1)}$-$[Sn_4Te_{12}]$).

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