5748 *Inorg. Chem.* **2010**, *49*, 5748–5752
DOI: 10.1021/ic100700f

Inorganic Chemistry
Article

Organotin Chalcogenide Salts: Synthesis, Characterization, and Extended Crystal Structures

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Received April 12, 2010

Reactions of Cl_3SnR^1H with Na_2E (E = Se, Te; $R^1 = C_2H_4COO$) in liquid ammonia afforded the salts of an anionic defect heterocubane, $[(RSn)_3Se_4]^-$ ($R = R^1$ and R^1H) or an $^1_\infty[(R^1Sn)_2Te_3{}^{2-}]$ anionic polymer, respectively. Although a reaction using a 1:1.5 ratio of $Cl_3SnR^1H{:}Na_2S\cdot 9H_2O$ in acetone/water produced a compound containing $[(R^1Sn)_3S_4]^{2-}$, a 1:2 ratio leads to the formation of $^1_\infty[(R^1Sn)_2S_3{}^{2-}]$, isostructural to the homologous Te species.

Introduction

The chemistry of Group 14 chalcogenidometallates has evolved with the development of several new synthetic methods that are constantly driven by the potential technological applications of these compounds, such as semiconductivity, photoconductivity, nonlinear optics, catalysis, and ion exchange capability.[1] Among these synthetic methods, the introduction of organic ligands with a designed functionality is shown to be a promising approach for a facile access to variety of new complexes with specific properties.[2] This may also provide an opportunity for combining different physical and chemical properties, tuning the cluster moiety and storing desirable information in the components by further organic reactions.

In our recent investigations, we focused on the synthesis and reactivity of ω-carbonyl-functionalized thiostannate cages of the general type $[(R^2Sn)_4(\mu\text{-}S)_6]$ ($R^2 = CMe_2CH_2COMe$) possessing a double-decker-like structure.[3] To understand the structural variety when changing to ω-carboxyl-ligated organotin chalcogenides, we have developed a facile approach to the synthesis of a new family of organotin sulfide-, selenide-, and telluride-based anions that formed upon a treatment of the 3-(trichlorostannyl)propanoic acid ($Cl_3SnC_2H_4COOH$) with Na_2E (E = S, Se, Te), either formed in situ or reacted as a salt. The anionic structural motifs of the resulting, organic-functionalized chalcogenidostannate complexes can be classified in two types: first, chalcogen-capped organotin chalcogenide six-membered rings, $[(R^1Sn)_3S_4]^{2-}$ in **1** ($R^1 = C_2H_4COO$) or $\{[R^1(R^1H)_2Sn_3Se_4][R^1{}_2(R^1H)Sn_3Se_4]\}^-$ in **2**, and second, organotin chalcogenide anionic polymers, $^1_\infty[(R^1Sn)_2E_3{}^{2-}]$ (E = S, in **3**; Te, in **4**). In the packing of the ions in the crystal, anions and cations are connected via coordination of the latter by oxygen donor atoms of R^1 and solvent molecules.

Experimental section

General. All synthesis steps were performed under Ar atmosphere. All solvents were dried and freshly distilled prior to use. Water was degassed by applying dynamic vacuum (1×10^{-3} mbar) for several hours. $Cl_3SnC_2H_4COOH$ was prepared according to a reported method.[4] Pure $Na_2S\cdot 9H_2O$, Se, and Te were purchased from Aldrich (>98%) and used as-received. ^1H NMR, ^{13}C NMR and ^{119}Sn NMR measurements were carried out using a Bruker DRX 400 MHz spectrometer at 25 °C. The chemical shifts were quoted in ppm relative to the residual protons of deuterated solvents in ^1H NMR and ^{13}C NMR. Me_4Sn was used as internal standard for ^{119}Sn NMR measurements. Infrared (IR) spectra were recorded on a Bruker IFS 88 spectrometer.

Synthesis of $[Na_2(MeOH)_{1.66}(H_2O)_{4.38}][(R^1Sn)_3S_4]$ (1). A solution of $Cl_3SnC_2H_4COOH$ (1.61 g, 5.4 mmol) in acetone (5.5 mL) was added very slowly to the solution of $Na_2S\cdot 9H_2O$ (1.94 g, 8.1 mmol) in acetone/water (20 mL, 1:1) at −5 °C. The mixture was stirred for 12 h at room temperature. The product was filtered and dissolved in methanol. Colorless crystals were obtained within two days by layering of the methanol solution by diethylether. Yield: 0.980 g (1.116 mmol, 62%). Elemental anal. Calcd: C, 13.81; H, 3.13; S, 14.75. Found: C, 14.01; H, 2.99;

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Table 1. Crystallographic and Refinement Details of **1**−**4** at 100 K

	1	**2**·$3H_2O$	**3**·H_2O	**4**
empirical formula	$C_{10.65}H_{27.40}Na_2O_{12.04}S_4Sn_3$	$C_{20}H_{41}NaO_{17}Se_8Sn_6$	$C_6H_{26}Na_2O_{13}S_3Sn_2$	$C_{13}H_{36}Na_2O_{11}Sn_2Te_3$
fw (g mol^{-1})	878.52	1920.34	685.81	1034.58
crystal color and shape	colorless block	yellow plate	colorless block	red block
crystal size (mm^3)	0.30 × 0.24 × 0.15	0.12 × 0.10 × 0.07	0.27 × 0.21 × 0.03	0.20 × 0.10 × 0.04
radiation (λ /Å)	Mo K_α, 0.71073	Mo K_α, 0.71073	Mo K_α, 0.71073	Mo K_α, 0.71073
crystal system	monoclinic	triclinic	triclinic	triclinic
space group	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	18.845(4)	10.964(3)	10.894(3)	11.709(3)
b (Å)	20.121(6)	15.478(4)	18.901(4)	11.796(3)
c (Å)	15.805(4)	15.943(4)	34.253(7)	12.190(3)
α (deg)		102.34(3)	102.45(3)	76.13(3)
β (deg)	107.52(3)	106.15(3)	94.05(3)	88.96(3)
γ (deg)		105.18(3)	98.75(3)	73.80(3)
V /Å^3	5715(3)	2385(2)	6768(3)	1567.5(7)
Z	8	2	12	2
ρ_{calcd} (g cm^{-3})	2.042	2.674	2.019	2.192
μ(Mo Kα) (mm^{-1})	2.97	9.26	2.58	4.40
absorp corr type	numerical	multiscan	multiscan	multiscan
min/max transmission	0.672/0.811	0.559/0.657	0.231/0.430	0.351/0.488
2θ range (deg)	2.04−51.76	4.08−50.00	2.44−50.00	3.44−57.84
no. of measured reflns	32810	21630	52808	20507
R(int)	0.0587	0.0514	0.0640	0.1080
no. of ind. reflns/ind. reflns ($I > 2\sigma(I)$)	5541/4590	7899/6256	23533/14013	6080/4009
no. of params	298	475	1405	287
R_1 ($I > 2\sigma(I)$)/wR_2 (all data)	0.0354/0.0992	0.0294/0.0688	0.0422/0.0981	0.0380/0.0702
S (all data)	1.04	1.02	1.00	0.881
largest diff. peak/hole (e$^-$ Å^{-3})	1.11/−1.02	1.20/−0.94	1.84/−0.93	1.05/−1.20

S, 15.06. ^{1}H NMR (400 MHz, MeOD-d_4, 25 °C): δ 1.64 (t, 6H, CH_2), 2.45 (t, 6H, CH_2). ^{13}C NMR (100 MHz, MeOD-d_4, 25 °C): δ 25.85 (CH_2), 31.72 (CH_2), 182.58 (COO). ^{119}Sn NMR (149 MHz, MeOD-d_4, 25 °C): δ −113.38.

Synthesis of [Na(MeOH)$_2$][R^1(R^{1}H)$_2$Sn$_3$Se$_4$][R^1$_2$(R^{1}H)Sn$_3$Se$_4$]·3H$_2$O (2·3H$_2$O). Selenium (0.355 g, 4.5 mmol) was suspended in liquid ammonia (50 mL) at −78 °C. Sodium (0.207 g, 9 mmol) was added slowly to this mixture. After 3 h of stirring, $Cl_3SnC_2H_4COOH$ (0.894 g, 3 mmol) was added to the suspension. The suspension turned to a clear orange solution. The mixture was allowed to warm up to −33 °C and was refluxed for 2 h. The liquid ammonia was then allowed to vaporize during 8 h. The product was extracted by ethanol. The solution of **2** in methanol was layered by diethyl ether. Light yellow plates of compound **2**·$3H_2O$ crystallized within one week. Yield: 1.11 g (0.58 mmol, 58%). Elemental anal. Calcd: C, 12.51; H, 2.15. Found: C, 12.63; H, 2.07. ^{1}H NMR (400 MHz, MeOD-d_4, 25 °C): δ 1.74 (t, 6H, CH_2), 2.34 (t, 6H, CH_2). ^{13}C NMR (100 MHz, MeOD-d_4, 25 °C): δ 26.90 (CH_2), 32.49 (CH_2), 182.58 (COO). IR (Nujol mull in KBr and polyethylene windows): $\tilde{\nu}$ 2921 (s), 2724 (w), 1701 (w), 1561 (m), 1461 (s), 1377 (s), 1261 (w), 1229(w), 1097 (w), 1091 (w), 973 (w), 892 (m), 723 (m), 691 (m), 595 (w), 503 (w), 456 (w), 399 (w), 353 (m), 197 (w), 175 cm^{-1} (s).

Synthesis of [Na$_2$(H$_2$O)$_8$][(R^{1}Sn)$_2$S$_3$]·H$_2$O (3·H$_2$O). A solution of $Cl_3SnC_2H_4COOH$ (1.61 g, 5.4 mmol) in acetone (5.5 mL) was added very slowly to the solution of $Na_2S\cdot 9H_2O$ (2.59 g, 10.8 mmol) in acetone/water (20 mL, 1:1) at −5 °C. The mixture was stirred for 12 h. Colorless crystals of **3**·H_2O were obtained within 1 week by layering of an aqueous solution of the product by THF. Yield: 1.074 g (1.566 mmol, 58%). Elemental anal. Calcd: C, 10.51; H, 3.82; S, 14.03. Found: C, 10.79; H, 3.62; S, 14.40. ^{1}H NMR (400 MHz, D_2O, 25 °C): δ 1.71 (t, 4H, CH_2), 2.55 (t, 4H, CH_2). ^{13}C NMR (100 MHz, D_2O, 25 °C): δ 27.22 (CH_2), 31.88 (CH_2), 183.75 (COO). ^{119}Sn NMR (149 MHz, D_2O, 25 °C): δ −74.70. IR (KBr, Nujol mull in polyethylene windows): $\tilde{\nu}$ 3382 (s), 1565 (s), 1417 (m), 1382 (s), 1286 (m), 1262 (w), 1239 (m), 1115 (m), 1026 (w), 899 (m), 800 (w), 747 (w), 687 (m), 525 (w), 429 (w), 350 (s), 289 (w), 176 (w), 158 cm^{-1}(s).

Synthesis of [Na$_2$(MeOH)$_7$][(R^{1}Sn)$_2$Te$_3$] (4). Tellurium (0.570 g, 4.5 mmol) was suspended in liquid ammonia (50 mL) at −78 °C. Sodium (0.207 g, 9 mmol) was added slowly to this mixture. After 2 h of stirring, $Cl_3SnC_2H_4COOH$ (0.894 g, 3 mmol) was added to the suspension. The suspension turned to a clear red-brown solution. The mixture was allowed to warm to −33 °C and was refluxed for 3 h. The liquid ammonia was then allowed to vaporize during 8 h. The product was extracted by ethanol. Ethanol was removed in vacuo and the product was dissolved in methanol. The methanol solution of the product was layered by diethyl ether. Red blocks of compound **4** crystallized within 5 days. Yield: 0.96 g (0.93 mmol, 62%). Elemental anal. Calcd: C, 15.09; H, 3.51. Found: C, 14.96; H, 3.31. ^{1}H NMR (400 MHz, D_2O, 25 °C): δ 1.14 (t, 4H, CH_2), 2.34 (t, 4H, CH_2), 3.30 (s, methanol solvent). ^{13}C NMR (100 MHz, D_2O, 25 °C): δ 21.08 (CH_2), 34.16 (CH_2), 49.00 (CH_3OH), 182.57 (COO). IR (Nujol mull in KBr and polyethylene windows): $\tilde{\nu}$ 2922 (s), 2853 (w), 2344 (s), 2133 (w), 1675 (w), 1548 (s), 1461 (s), 1379 (s), 1291 (w), 1261 (w), 1180 (w), 1119 (m), 1067 (s), 970 (w), 916 (w), 723 (m), 673 (w), 481 (w), 464 (w), 353 (w), 174 cm^{-1} (s).

X-ray Structure Determination. Data were collected on a diffractometer equipped with a STOE imaging plate detector system IPDS2, using graphite-monochromized Mo K_α radiation (λ = 0.71073 Å) at 100 K. Structure solution and refinement were performed by direct methods and full-matrix least-squares on F^2, respectively, using ShelxTL software.[5] Where possible, H atoms were inserted assuming idealized geometry and refined as riding on their parent atoms (with $U_{eq} = nU_{eq}$(parent atom), where n = 1.2 for H atoms of methylene groups and phenyl rings; n = 1.5 for H atoms of methyl groups). The H atoms of the carboxyl groups (in **2**) were found on the difference Fourier map and refined with $U_{eq} = 1.5U_{eq}$ (carboxyl O atom). The same treatment was applied to H atoms of water molecules (in **2** and **3**). Restraints were imposed on the O−H bond lengths at 0.84 Å. Subsequently, all H atoms parameters were constrained (for hydroxyl H atoms AFIX 147 constraint was used). Final crystallographic data and values of R_1 and wR_2 are listed in Table 1. Selected bond lengths and bond angles are provided in Tables S1−S4 in the Supporting Information. Further comments concerning refinement and specific crystallographic problems are available in the Supporting Information.

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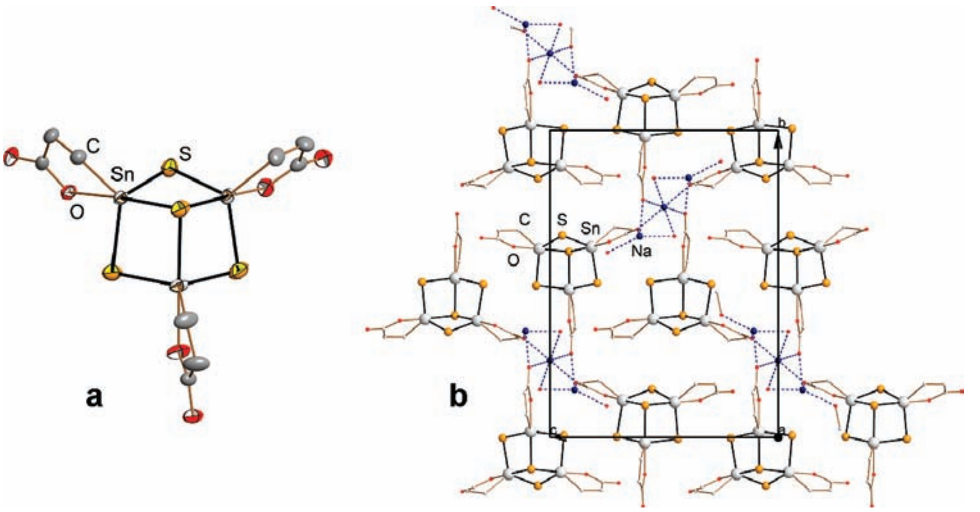


Figure 1. (a) Thermal ellipsoid plot (40% probability) of the anionic unit in **1**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Sn−S, 2.405(2)−2.593(2); Sn−C, 2.138(5)−2.146(5); Sn−O, 2.209(4)−2.236(4). (b) Network of the packing of anions and cation aggregates in **1** along the crystallographic *a* axis. Disordered sodium atoms, methanol molecules, and hydrogen atoms are omitted for clarity.

UV−Visible spectra. UV−vis spectra were recorded on a Perkin-Elmer Cary 5000 UV/vis/NIR spectrometer in the range of 800−200 nm employing double beam technique. The sample was prepared as suspension in Nujol oil between two quartz plates and brought into the UV−vis beam.

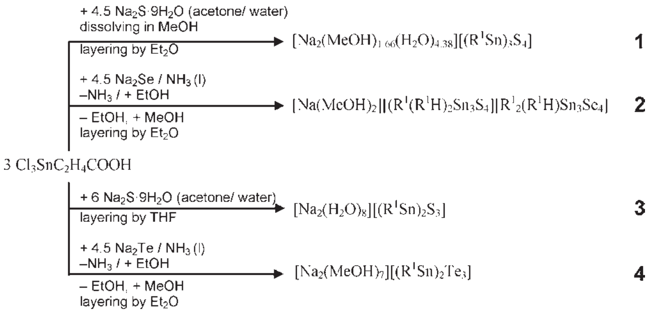
Results and Discussion

Syntheses. Compounds **2**$\cdot$3H_2O and **4** are synthesized by the reaction of $Cl_3SnC_2H_4COOH$ with in situ prepared Na_2Se and Na_2Te in liquid ammonia, respectively. After evaporation of the ammonia, the residues have been extracted with ethanol. Layering of the methanol solutions by diethylether, compounds **2**$\cdot$3H_2O or **4** were received as yellow or red crystals within 5 days or 1 week, respectively. By the reaction of $Cl_3SnC_2H_4COOH$ with $Na_2S\cdot 9H_2O$ (1:1.5) in a mixture of acetone/water, and ensuing layering of methanol solution by diethylether, compound **1** was synthesized and received as colorless single crystals. Increasing the ratio of $Cl_3SnC_2H_4COOH$/$Na_2S\cdot 9H_2O$ to 1:2, results in the formation of compound **3**$\cdot H_2O$, which was crystallized by layering of an aqueous solution of the crude product by THF (Scheme 1).

Crystal Structures. Compounds $[Na_2(MeOH)_{1.66}(H_2O)_{4.38}][(R^1Sn)_3S_4]$ (**1**), $[Na(MeOH)_2][R^1{}_2(R^1H)Sn_3Se_4][R^1(R^1H)_2Sn_3Se_4]\cdot 3H_2O$ (**2**$\cdot$3H_2O), $[Na_2(H_2O)_8][(R^1Sn)_2S_3]\cdot H_2O$ (**3**$\cdot H_2O$), and $[Na_2(MeOH)_7][(R^1Sn)_2Te_3]$ (**4**) were characterized spectroscopically and by means of X-ray diffraction.

The anion in **1** is isostructural to the one observed in recently reported $[Na_2(EtOH)_3][(R^1Sn)_3S_4]$,[3c] representing a distorted defect heterocubane, a so-called “semicube”, with one R^1Sn corner missing (Figure 1a). However, the cited compound was synthesized in NH_3/EtOH, thus similar to the synthesis of compounds **2** and **4** herein. Accordingly, the counterion coordination sphere in **1**, which contains MeOH and H_2O instead of EtOH molecules, is different. Regarding the connection of anions and cation aggregates in **1**, an infinite, two-dimensional layer results (Figure 1b). The interatomic distances and angles of the anion in **1** are very similar to those observed in the cited compound.

Scheme 1. Synthesis of Compounds **1**−**4**. More Details on the Work-up Procedures Are Provided in the Experimental Section; R^1 = C_2H_4COO



The asymmetric unit of compound **2** is shown in Figure 2a. The anions represent $[(RSn)_3Se_4]$ semicube structural motifs. While the topology itself is already known from polymeric selenidostannates,[6] **2** is the first example containing isolated anions with terminal organic ligands instead of Se bridges. One asymmetric unit of **2** consists of two different types of semicube building units: an anionic unit $[R^1{}_2(R^1H)Sn_3Se_4]^-$, ligated by two R^1 and one R^1H groups, and a neutral semicube $[R^1(R^1H)_2Sn_3Se_4]$, ligated by one R^1 and two R^1H groups. These building units are linked by one Na^+ cation per formula unit to form a one-dimensional, comblike coordination polymer, $\{[Na(MeOH)_2][R^1{}_2(R^1H)Sn_3Se_4][R^1(R^1H)_2Sn_3Se_4]\cdot 3H_2O\}$ (Figure 2b). The one-dimensional chains are further connected via hydrogen bonding interactions including water molecules (see Figures S1 and S2 in the Supporting Information).

The isostructural anions in compounds **3** and **4** represent an unprecedented, one-dimensional polymer moiety, ${}^1_\infty[(R^1Sn)_2E_3{}^{2-}]$ (E = S in **3**, Te in **4**). In the crystal, the

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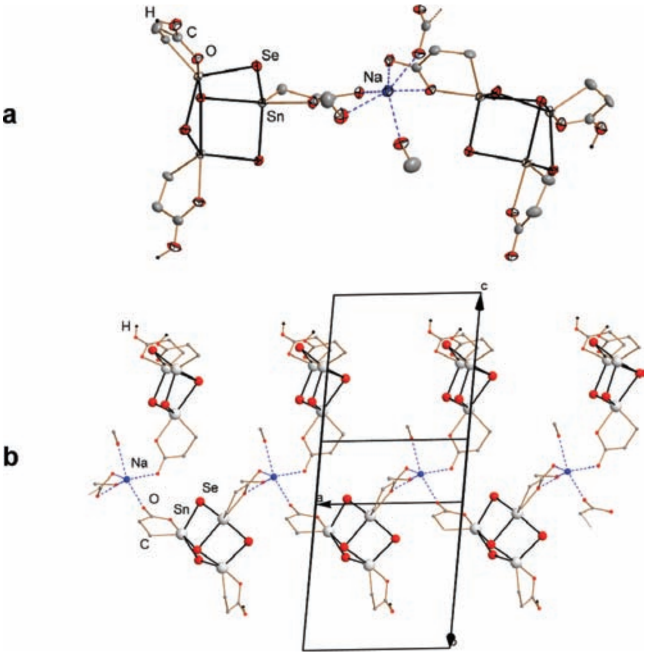

Figure 2. (a) Thermal ellipsoid plot (40% probability) of the asymmetric unit in **2**. Water molecules and hydrogen atoms (except those of the carboxyl groups) are omitted for clarity. Selected bond lengths [Å]: Sn−Se, 2.5257(10)−2.7616(12); Sn−C, 2.133(7)−2.151(7); Sn−O, 2.218(5)−2.271(5); Na···O, 2.383(5)−-2.469(5). (b) One dimensional comblike chain by coordination of the anionic units in **2** to Na$^+$ ions. Water molecules and hydrogen atoms (except those of the carboxyl groups) are omitted for clarity.

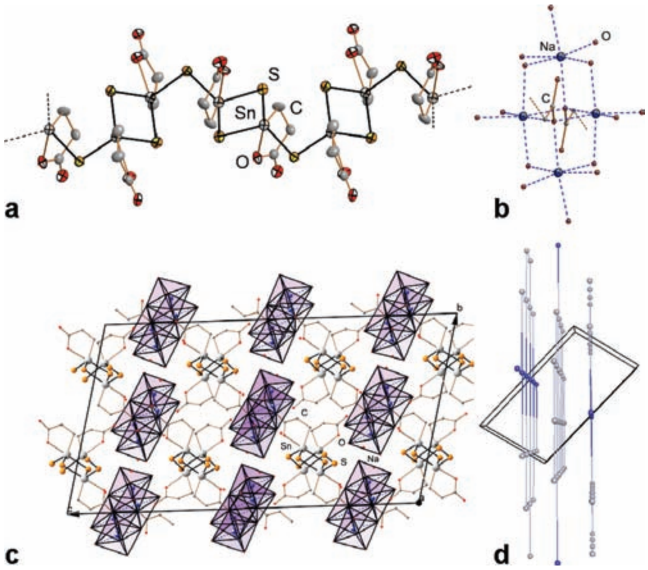

Figure 3. (a) Fragment of the $^1_\infty[(R^1Sn)_2S_3{}^{2-}]$ chain in **3**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids have been drawn at the 40% probability level. Selected bond lengths [Å]: Sn−S, 2.401(2)−2.530(2); Sn−C, 2.131(7)−2.170(7); Sn−O, 2.280(5)−2.452(5). (b) Coordination aggregate of Na$^+$ ions within the $[Na_4O_{16}]$ complex unit. (c) Layers perpendicular to [100] in **3**. Hydrogen atoms are omitted for clarity. (d) View of the simplified net along the crystallographic *a* axis.

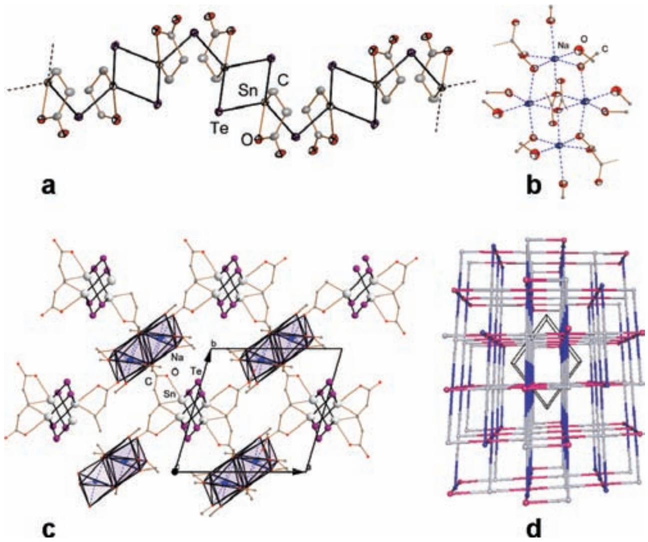

Figure 4. (a) Fragment of the $^1_\infty[(R^1Sn)_2Te_3{}^{2-}]$ chain in compound **4**. Thermal ellipsoids have been drawn at the 40% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Sn−Te, 2.7273(10)−2.8252(11); Sn−C, 2.129(8)−2.184(8). (b) Coordination aggregate of Na$^+$ ions within the $[Na_4O_{16}]$ complex unit. (c) Linkage of anionic chains and cation aggregates parallel to the *ab* plane of **4**. Hydrogen atoms are omitted for clarity. (d) View of the simplified net along the crystallographic *c* axis.

polymeric chains are surrounded and connected by sodium cations to form extended network structures. In both compounds, the cationic linkers seem to adopt the optimal size and shape for maximum lattice energy by forming a complex aggregate of two face-linked Na_3O_4 semicubes, with additional external O ligands, to represent a $[Na_4O_{16}]$ unit.

The Sn/S polymer in **3** (Figure 3a) is composed of four-membered rings $(R^1Sn)_2S_2$ that are linked by μ-S bridges, thus representing corner-sharing $[R^1{}_2Sn_2S_4]^{2-}$ units. The Sn−S bond lengths are in the common range.[7] The cationic part in **3** (Figure 3b) consists of four six-coordinated sodium atoms which are linked by two types of bridging O atoms, namely four four-coordinated oxygen atoms of the solvent water in $Na\cdots OH_2\cdots Na$ bridges [Na···O 2.380(7)−2.484(6) Å], and two four-coordinated oxygen atoms in $Na_3\cdots O{-}C$ bridges [Na···O 2.349(6)−2.520(6) Å]. The remaining sites around the sodium atoms are occupied by ten oxygen atoms of solvent water molecules. The infinite, two-dimensional layer observed in **3** (Figure 3c) possesses the very common sql ($4^4.6^2$) topology (Figure 3d), as determined by the program package TOPOS.[8]

Although comprising the same (RSn)/E polymer type, a three-dimensional network is formed by the anionic chains of corner-sharing $[(R^1Sn)_2Te_4]^{2-}$ units (Figure 4a), and the connecting $[Na_4O_{16}]$ aggregates (Figure 4b) in **4**. Sn−Te bond lengths are within the known range.[9] As shown in Figure 4b, the four six-coordinated sodium cations within the complex $[Na_4O_{16}]$ aggregate are again linked by two types of bridging O atoms. Four oxygen atoms of solvent methanol molecules are four-coordinated in $Na\cdots OH({-}C)\cdots Na$ bridges [Na···O 2.335(7)−2.541(6) Å], whereas two four-coordinated oxygen atoms are involved in $Na_3\cdots O{-}C$ bridges [Na···O 2.309(6)−2.622(7) Å]. Eight oxygen atoms of solvent methanol

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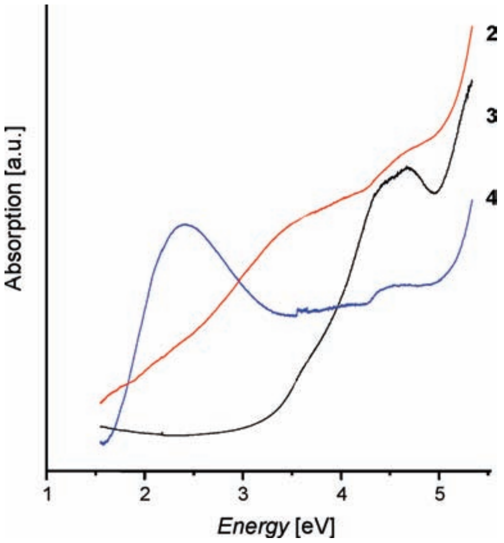

Figure 5. Solid-state UV−visible spectra of compounds **2**·3H_2O, **3**·H_2O, and **4**, recorded as suspensions of single crystals in nujol oil (see Experimental Section).

molecules and two oxygen atoms of COO^- groups of the propanoic acid substituents serve to complete the coordination environment around the sodium cations.

The topology in compound **4** accords to a uninodal 4-connected 3D net with a Schläfli symbol of $6^4.8^2$ (NbO-type topology).[8] Figure 4c illustrates the linkage of anionic chains, running along [0 0 1], and cationic aggregates within the *ab* plane of **4**. The resulting 3D network is sketched in Figure 4d.

Optical Absorption Behavior. UV−visible spectra of compounds **2**·3H_2O, **3**·H_2O, and **4** (Figure 5) illustrate both the different structural features and the different chalcogenide ligands involved. Compounds **3**·H_2O and **4** show similar signatures, an onset of absorption at 3.2 eV (387 nm, in **3**) or 1.6 eV (775 nm, in **4**), followed by a broad maximum around 4.7 eV (264 nm, in **3**) or 2.4 eV (517 nm, in **4**), in good agreement with the visible color (colorless (**3**) or red (**4**), respectively) of the compounds. The absorption can be assigned to p(S,Te) → p(Sn) charge transfer processes, according to similar values reported for further Sn/E complexes.[10] For compound **2**·3H_2O, exhibiting another structural motif, the onset of absorption is much smoother, becoming steeper around 2.5 eV (496 nm) and leading to a first plateau around 3.3 eV (376 nm) in accordance with the light yellow appearance of the crystals. All three compounds show a second onset of absorption around 4.3 eV (288 nm), assignable to p(O) → p(Sn) charge transfer involving the organic ligand,[11] which is supposed to be similar for all compounds.

Summary

As can be gathered from the above discussion, reactions of 3-(trichlorostannyl)propanoic acid with Na_2E (E = S, Se, Te) afforded different organotin chalcogenide salts, depending on (a) the chalcogenide used, (b) the (RSn):E ratio at the reaction, and (c) the solvent/work up procedure. The observed (RSn)/E anions accord to one of two different structural motifs. Using S or Se, $(RSn)_3E_4$ semicubes form the base of the anionic parts, whereas with E = Te, an organotin chalcogenide polymer chain is obtained. The same polymer type is also observed with E = S when increasing the amount of Na_2S. Although it has not been possible yet to explain why a particular anionic structure forms under the given condition rather than another one, it is obvious that the best fit between anions and cations will result in maximum lattice energy, and will thus decide about the crystalline product observed. In addition, not only the type of the chalcogen used, but also the available solvent molecules contributing to the coordination environment around the sodium cations influence the topology of the resulting network of anions and cations within the crystal. UV−visible spectra of compounds **2**·3H_2O, **3**·H_2O, and **4** illustrated the presence of both different structural motifs and different chalcogenide ligands.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft (DFG).

Supporting Information Available: CIF files for **1**−**4**. Details on crystal structure refinement, atom labeling scheme (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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