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Zinc Tin Chalcogenide Complexes and Their Evaluation as Molecular Precursors for Cu₂ZnSnS₄ (CZTS) and Cu₂ZnSnSe₄ (CZTSe)

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S Supporting Information

ABSTRACT: A series of five heteronuclear zinc tin chalcogenide complexes with the general formula $[(\text{tmeda})\text{Zn}(\text{SnR}_2)_2\text{E}_3]$ (1-R, E = S; R = Me, Ph, tBu; 2-R, E = Se; R = Ph, tBu) have been synthesized and characterized by X-ray crystal structure analysis. In all cases, the six-membered ZnSn₂E₃ rings exhibit twist boat conformation. The presence of the molecular structures in solution is confirmed by ¹¹⁹Sn and ⁷⁷Se NMR spectroscopy. Cothermolysis experiments using a mixture of complexes 1-R or 2-R and $[(iPr_3PCu)_2(EC_2H_4E)]_2$ as a copper source were monitored by thermogravimetry and temperature dependent X-ray powder diffraction to examine the thermolysis reaction. According to Rietveld refinement, the solid residue consists of Cu_2ZnSnS_4 (up to 78 wt %) or $Cu_2ZnSnSe_4$ (up to 43 wt %) as the main product, respectively.



INTRODUCTION

 Cu_2ZnSnS_4 (CZTS) is a direct band gap semiconductor with a band gap near 1.45 eV and a high absorption coefficient above 10^4 cm⁻¹. Therefore, Cu₂ZnSnS₄ is one of the most promising materials for solar cell applications, especially in thin film solar cells.¹ CZTS is found as a mineral in the earth's crust known as kesterite in which Zn^{2+} can be replaced by Fe^{2+} . In comparison to common absorber materials for thin film solar cells like CdTe, GaAs, or CuInSe₂, CZTS does not contain any toxic elements, and all elements are highly abundant in the earth's crust. The first CZTS based solar cell was introduced by H. Katagiri² and co-workers in 1997 who used electron beam evaporation of the elements to form a mixed layer of copper, zinc, and tin on a molybdenum coated glass substrate. Sulfurization in an H₂S atmosphere resulted in a thin film of CZTS as p-type absorber layer. The p-n-junction was generated by a thin layer of n-type cadmium sulfide; aluminum doped zinc oxide was used as an electric contact. In this photovoltaic cell a conversion efficiency of 0.66% was achieved. The general setup of a CZTS solar cell was preserved until today, but for the deposition of the CZTS layer several methods were suggested. Besides expensive high vacuum based methods for deposition of mixed metal layers such as electron beam evaporation,³⁻⁷ thermal evaporation⁸⁻¹¹ and sputtering, $^{12-18}$ also nonvacuum based methods have been reported. Electrochemical deposition $^{19-25}$ or sol-gel $^{26-29}$ methods were used to deposit the metals or metal salts on a substrate followed by heating in sulfur vapor or H₂S atmosphere to form CZTS. First spray pyrolysis experiments for depositing a CZTS layer were performed by Nakayama and Ito starting from a solution of CuCl, ZnCl₂, SnCl₄, and thiourea in water/ethanol in 1996. A further sulfurization step was necessary to obtain a stoichiometric CZTS layer.³⁰

For deposition of CZTS and CZTSe thin films with high power conversion efficiency, low-cost solution based methods

have been recently developed. By deposition from hydrazine based solutions of Cu₂S, Zn, SnSe, S, and Se, conversion efficiencies above 12% were reported.³¹ To replace toxic and explosive hydrazine, a solvent system combining alkyl amines and alkyl thiols has been established that dissolves metal chalcogenides as well as pure metals at room temperature and is successfully applied for the deposition of CZTS from solution.^{32,33}

A possibility to adjust the element ratio in the precursor solution could be the use of a soluble single-source precursor compound with the elements incorporated in the required stoichiometric ratio. The reduction of the four component system to a three component system was possible by using thiourea,³⁴ xanthate,³⁵ or dithiocarbamate³⁶ complexes of copper, zinc, and tin for spray pyrolysis or aerosol assisted chemical vapor deposition (AACVD). Controlling the stoichiometric composition of CZTS with this kind of methods is difficult; therefore, the further reduction to a two component system has been suggested, but only a few examples for complexes containing a Zn-S-Sn structural motif are known in the literature. Most publications concerning Sn/Zn/S compounds are about cluster anions $[{\rm Zn}_4{\rm Sn}_4{\rm S}_{17}]^{\bar{1}0-\ 37-39}$ or $[Zn_5Sn_5S_{20}]^{10-40}$ with alkali metal counterions. These ionic species are not suitable as molecular precursors for CZTS since the cations cannot be eliminated during thermolysis. Examples for neutral complexes are $[(RSn)_4(Zn_8X_8)S_{10}]$ with X = Cl⁻, Br⁻, I⁻, and R = organic group,⁴¹ [$\{1,3-C_6H_4(PhPS)_2CSnEt_2\}$ - $(\mu$ -ZnS)]₂ which could be isolated in low yield and as a mixture with other products only,⁴² and the tren stabilized mixed zinc tin sulfide $[{(tren)Zn}_2(\mu-Sn_2S_6)]$ (tren = tris(2-aminoethyl)amine) which was synthesized under solvothermal conditions.⁴³

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Herein we present the synthesis and characterization of a series of five mixed metal zinc tin chalcogenide complexes $[(\text{tmeda})\text{Zn}(\text{SnR}_2)_2\text{S}_3]$ (1-R, R = Me, Ph, *t*Bu) and $[(\text{tmeda})\text{-Zn}(\text{SnR}_2)_2\text{Se}_3]$ (2-R, R = Ph, *t*Bu). Preliminary studies of cothermolysis reactions of 1-Me, 1-Ph, or 2-*t*Bu together with $[(iPr_3PCu)_2(\text{SC}_2H_4\text{S})_2]$ or $[(iPr_3PCu)_2(\text{SeC}_2H_4\text{Se})_2]$ yield Cu₂ZnSnS₄ or Cu₂ZnSnSe₄, respectively, as main products.

EXPERIMENTAL SECTION

All syntheses were performed by applying a Schlenk technique or in an MBRAUN UniLab glovebox with N₂ as inert gas. All solvents and tmeda were dried according to common methods and distilled prior to use. Zn(OAc)₂·2H₂O was dehydrated with Ac₂O, R₂Sn(OAc)₂ (R = Me, Ph, tBu) was prepared by the reaction of (R₂SnO)₃ in a 2:1 mixture of acetic acid and Ac₂O⁴⁴⁻⁴⁶ and recrystallized from *n*-heptane.⁴⁷ While (Ph₂SnO)₃ is commercially available, (Me₂SnO)₃ and (tBu₂SnO)₃ were synthesized starting from Me₂SnCl₂ and tBu₂SnCl₂ (obtained by the reaction of SnCl₄ with tBuMgCl⁴⁸) in aqueous NH₃.^{49,50} (Me₃Si)₂E (E = S, Se) was prepared by reaction of Na₂E (obtained by the reactions of the elements in liquid NH₃⁵¹) and Me₃SiCl.⁵² [(*i*Pr₃PCu)₂(Sc₂H₄S)]₂⁵³ and [(*i*Pr₃PCu)₂(SeC₂H₄Se)]₂⁵⁴ were prepared according to published procedures.

NMR spectra were measured using a Bruker Avance DPX-400 spectrometer with 400 MHz proton frequency in dried and distilled THF- d_8 as solvent. ¹H NMR spectra were referenced to TMS as an internal standard. Heteronucleus NMR spectra were referenced using the \pm -scale.⁵⁵ Elemental analyses (C, H, N) were measured with a Heraeus Vario El, TG/DTA analysis with a Netzsch STA 449 F1 (argon as carrier gas; flow rate 25 mL/min; heating rate 10 K/min) coupled to an Aëolos QMS 403 D mass spectrometer. Scanning electron microscopy was performed on a leo gemini device equipped with an Oxford Instruments 7426 EDX detector.

[(tmeda)Zn(SnMe₂)₂S₃] (1-Me). A 734 mg (4 mmol) portion of Zn(OAc)₂ was suspended in 40 mL of DME. A 1.2 mL (8 mmol) portion of tmeda and 1.69 mL (8 mmol) of (Me₃Si)₂S were added successively. The colorless solution was cooled to 0 °C, and 1.066 g (4 mmol) Me₂Sn(OAc)₂ dissolved in 20 mL of DME was added. After the solution was warmed to room temperature within 2 h, the solvent was reduced to half the volume. Storage for 16 h at -25 °C gave 350 mg (0.61 mmol, 30%) of 1-Me as colorless blocks. ¹H NMR (400 MHz, THF-*d*₈, 25 °C, TMS): δ = 0.53 (12H, s, ²J_{H117Sn} = 57.5 Hz, ²J_{H119Sn} = 60 Hz, Sn-CH₃), 2.51 (12H, s, N-CH₃), 2.67 (4H, s, N-CH₂). ¹¹⁹Sn{¹H} NMR (149 MHz, THF-*d*₈, 25 °C, TMS): δ = 122 (²J_{119Sn17Sn} = 184 Hz, ¹J_{119SnC} = 387 Hz). ¹³C{¹H} NMR (100 MHz, THF-*d*₈, 25 °C, TMS): δ = 3.1 (¹J_{C117Sn} = 370 Hz, ¹J_{C119Sn} = 387 Hz, Sn-CH₃), 47.2 (N-CH₃), 56.5 (N-CH₂). Anal. Calcd (%) for C₁₀H₂₈N₂S₃Sn₂Zn: C 20.9, H 4.9, N 4.9. Found: C 20.8, H 4.8, N 4.8.

[(tmeda)Zn(SnPh₂)₂S₃] (1-Ph). A 367 mg (2 mmol) portion of Zn(OAc)₂ was suspended in 20 mL of DME. A 0.6 mL (4 mmol) portion of tmeda and 0.85 mL (4 mmol) of (Me₃Si)₂S were added successively. The colorless solution was cooled to -70 °C, and 781 mg (2 mmol) of Ph₂Sn(OAc)₂ dissolved in 10 mL DME was added at -70 °C. After the solution was warmed to room temperature within 2 h, the solvent was reduced to ca. 10 mL. Storage for 2 days at 2 °C gave 600 mg (0.73 mmol, 73%) of 1-Ph as colorless plates. ¹H NMR (400 MHz, THF-*d*₈, 25 °C, TMS): δ = 2.18 (12H, s, N–CH₃), 2.53 (4H, s, N–CH₂), 7.23 (12H, m, *m*- + *p*-H SnPh₂), 7.68 (8H, m, ²J_{H117/119Sn} = 62 Hz, *o*-H SnPh₂). ¹¹⁹Sn{¹H} NMR (149 MHz, THF-*d*₈, 25 °C, TMS): δ = 24 (²J_{119Sn117Sn} = 178 Hz, ¹J_{119SnC} = 595 Hz). Anal. Calcd (%) for C₃₀H₃₆N₂S₃Sn₂Zn: C 43.8, H 4.4, N 3.4. Found: C 43.6, H 4.2, N 3.7.

[(tmeda)Zn(SntBu₂)₂S₃] (1-tBu). A 367 mg (2 mmol) portion of $Zn(OAc)_2$ was suspended in 25 mL of DME. A 0.6 mL (4 mmol) portion of tmeda and 0.85 mL (4 mmol) of (Me₃Si)₂S were added successively. The colorless solution was cooled to -40 °C, and 702 mg (2 mmol) of $tBu_2Sn(OAc)_2$ dissolved in 10 mL of DME was added at -40 °C. After warming the solution to room temperature within 3 h and stirring for 1 h at room temperature, the solvent was reduced to

ca. 10 mL. Storing for 3 days at 2 °C gave 400 mg (0.54 mmol, 54%) **1-tBu** as colorless plates. ¹H NMR (400 MHz, THF- d_{s} , 25 °C, TMS): $\delta = 1.29$ (36H, s, ³ $J_{H1175n} = 81$ Hz, ³ $J_{H1195n} = 84$ Hz, Sn–C–(CH₃)₃), 2.54 (12H, s, N–CH₃), 2.66 (4H, s, N–CH₂). ¹¹⁹Sn{¹H} NMR (149 MHz, THF- d_{s} , 25 °C, TMS): $\delta = 132$ (² $J_{1195n1175n} = 158$ Hz, ¹ $J_{1195nC} =$ 412 Hz). Anal. Calcd (%) for C₂₂H₅₂N₂S₃Sn₂Zn: C 35.5, H 7.0, N 3.8. Found: C 35.2, H 6.9, N 3.7.

[(tmeda)Zn(SnPh₂)₂Se₃] (2-Ph). A 367 mg (2 mmol) portion of Zn(OAc)₂ was suspended in 25 mL of DME. A 0.6 mL (4 mmol) portion of tmeda and 1.00 mL (4 mmol) of (Me₃Si)₂Se were added successively at 0 °C. The colorless solution was cooled to -50 °C, and 781 mg (2 mmol) of Ph₂Sn(OAc)₂ dissolved in 10 mL of DME was added at -50 °C. The solution was warmed to room temperature within 1 h and stirred for 30 min. The solvent was reduced to ca. 10 mL. Storage for 3 days at -25 °C gave 200 mg (0.21 mmol, 21%) of 2-Ph as colorless plates. ¹H NMR (400 MHz, THF-*d*₈, 25 °C, TMS): δ = 2.23 (12H, s, N–CH₃), 2.55 (4H, s, N–CH₂), 7.24 (12H, m, *m*+ *p*-H SnPh₂), 7.69 (8H, m, ²J_{H117/119Sn} = 62 Hz, *o*-H SnPh₂). ¹¹⁹Sn^{{1}H} NMR (149 MHz, THF-*d*₈, 25 °C, TMS): δ = -651 (¹J_{119Sn77Se} = 1580 Hz, ¹J_{119Sn17Sn} = 215 Hz). ⁷⁷Se^{{1}H} NMR (76 MHz, THF-*d*₈, 25 °C, TMS): δ = -531 (¹J_{77Se119Sn} = 1580 Hz, Zn–Se–Sn), Anal. Calcd (%) for C₃₀H₃₆N₂-Se₃Sn₂Zn: C 37.4, H 3.8, N 2.9.

[(tmeda)Zn(SntBu₂)₂Se₃] (2-tBu). A 367 mg (2 mmol) portion of Zn(OAc)₂ was suspended in 50 mL of DME. A 0.6 mL (4 mmol) portion of tmeda and 1.00 mL (4 mmol) of (Me₃Si)₂Se were added successively at 0 °C. The colorless solution was cooled to -50 °C, and 702 mg (2 mmol) of tBu₂Sn(OAc)₂ dissolved in 10 mL of DME was added at -50 °C. A colorless solid precipitated. The suspension was warmed up to room temperature and stirred for 1 h. The clear solution was concentrated to ca. 50 mL. Storage for 2 days at -25 °C gave 250 mg of crystals of (tBu₂SnSe)₂. After filtration the volume of the colorless solution was reduced to ca. 20 mL. Storing the solution for 2 days gave 250 mg (0.28 mmol, 28%) of 2-tBu as yellow plates. ¹H NMR (400 MHz, THF- d_8 , 25 °C, TMS): $\delta = 1.26$ (36H, s, ${}^{3}J_{H117Sn} =$ 82 Hz, ${}^{2}J_{H119Sn}$ = 84 Hz, Sn-C-(CH₃)₃), 2.54 (12H, s, N-CH₃), 2.66 $(4H, s, N-CH_2)$. ¹¹⁹Sn{¹H} NMR (149 MHz, THF- d_{8} 25 °C, TMS): $\delta = 102 ({}^{1}J_{119\text{Sn77Se}} = 1597 \text{ Hz}, {}^{1}J_{119\text{Sn77Se}} = 1390 \text{ Hz}, {}^{2}J_{119\text{Sn117Sn}} = 160$ Hz). ⁷⁷Se{¹H} NMR (76 MHz, THF- d_8 , 25 °C, TMS): $\delta = -631$ ${}^{(1)}_{775e1175n} = 1527 \text{ Hz}, {}^{11}_{775e1195n} = 1597 \text{ Hz}, \text{ Zn-Se-Sn}), -583 \\ {}^{(1)}_{775e1175n} = 1327 \text{ Hz}, {}^{11}_{775e1195n} = 1390 \text{ Hz}, \text{ Sn-Se-Sn}). \text{ Anal. Calcd} \\ (\%) \text{ for } C_{22}H_{52}N_2Se_3Sn_2Zn: C 29.9, H 5.5, N 3.2. Found: C 28.9, H \\ \end{array}$ 4.8, N 3.8.

X-ray Crystal Structure Analysis. Crystallographic data are given in Table S1 (Supporting Information). Measurements were performed using a STOE IPDS or STOE IPDS 2T image plate diffractometer system equipped with a sealed Mo X-ray tube and a graphite monochromator crystal (λ (Mo K α) = 71.073 pm). Data reduction and numerical absorption correction were done with STOE X-AREA software.⁵⁶ All structures were solved by direct methods using SHELXS-2014 and refined with SHELXL-2014.57 All non-hydrogen atoms (besides disordered C atoms of the tmeda ligand in 1-tBu, of the tmeda ligand and one tBu group in 2-tBu) were refined with anisotropic thermal parameters; hydrogen atoms were included on idealized positions applying the riding model. Diamond 3.2k was used for visualization of the crystal structures.⁵⁸ CCDC 1555378-1555382 contain the crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

The PXRD measurements were carried out on a STOE STADI-P diffractometer equipped with a sealed Cu X-ray tube and a germanium(111) monochromator crystal (λ (Cu K α 1) = 154.060 pm). Samples of the air sensitive complexes were prepared in a glovebox under N₂ atmosphere, filled in glass capillaries (Hilgenberg, outer diameter 0.5 mm), and measured in Debye–Scherrer mode. The thermolysis products were measured as flat samples between two acetate films in transmission mode. Rietveld analyses of the diffraction patterns were performed with Bruker TOPAS 5 software⁵⁹ using the fundamental parameter approach. Crystal structure data for

 Cu_2ZnSnS_4 ,⁶⁰ ZnS (sphalerite),⁶¹ SnS,⁶² Cu_2S (tetragonal⁶³ and monoclinic⁶⁴), $Cu_2ZnSnSe_4$,⁶⁵ ZnSe,⁶⁶ SnSe,⁶⁷ Cu_2Se ,⁶⁸ and Cu_2SnSe_4 ,⁶⁹ were taken from literature reports.

RESULTS AND DISCUSSION

Synthesis. The heteronuclear complexes **1-R** and **2-R** (R = Me, Ph, *t*Bu) are formed in one-pot reactions starting from $Zn(OAc)_2$, tmeda, $E(SiMe_3)_2$ (E = S, Se), and $R_2Sn(OAc)_2$ (Scheme 1). Intermediates are tmeda stabilized zinc chalcoge-

Scheme 1. Syntheses of the Zinc Tin Chalcogenide Complexes 1-R and 2-R



nide complexes $[(\text{tmeda})\text{Zn}(\text{ESiMe}_3)_2]$ (E = S, Se) reported by DeGroot and Corrigan.⁷⁰ These complexes were already used as starting materials for the formation of ternary nanoclusters like $[\text{Zn}_x\text{Cd}_{10-x}\text{E}_4(\text{EPh})_{12}(\text{PnPr}_3)_4]^{71}$ (E = Se, Te) or $[(\text{tmeda})_6\text{Zn}_{14-x}\text{Mn}_x\text{S}_{13}\text{Cl}_2]$ (E = S, Se).^{72,73} The reaction of $[(\text{tmeda})\text{Zn}(\text{ESiMe}_3)_2]$ with stoichiometric amounts (ratio SiMe₃/OAc = 1/1) of diorganotin acetates Me₂Sn(OAc)₂, Ph₂Sn(OAc)₂, and *t*Bu₂SnOAc₂ (Scheme 1) yields trinuclear zinc tin sulfide and selenide complexes **1-R** and **2-R**. These compounds are stable in solution for some time but decompose slowly under formation of organotin chalcogenides and ZnS or ZnSe, respectively.

Single Crystal Structure Analysis. All complexes 1-R and 2-R could be characterized by single crystal X-ray structure analysis (Table S1). They are isostructural with a six-membered ring consisting of one zinc, two tin, and three chalcogen atoms. The tmeda ligand chelating the zinc atoms and the organic groups R binding to tin atoms complete the tetrahedral coordination of the metal atoms.

As examples for the structure motif the structures of both complexes containing SnPh_2 units, **1-Ph** and **2-Ph**, are shown in Figure 1. Whereas **1-Ph** crystallizes in the triclinic space group $P\overline{1}$ (z = 2), **2-Ph** crystallizes in the monoclinic space group C2/

c (z = 4). In 2-Ph, Zn1 and Se1 are located on the 2-fold axis: Half of the molecule forms the asymmetric unit, whereas in 1-Ph both SnPh₂ groups differ in the orientation of the phenyl groups binding to Sn1 and Sn2. Also, in 1-Me which crystallizes in the orthorhombic space group C222₁, the molecule contains a crystallographic 2-fold axis; the other complexes are only approximately C_2 symmetric. Both complexes containing SntBu₂ units, 1-tBu and 2-tBu, form isomorphous crystals with space group $P2_1/n$ (z = 4).

On the basis of the torsion angles, in all complexes the sixmembered $ZnSn_2E_3$ rings are in twist boat conformation. The larger selenium atoms in **2-Ph** and **2-tBu** widen the bond lengths (Table 1) to the metal atoms by 12 ± 1 pm in agreement with the difference in covalent radii (S 104 pm; Se 117 pm).⁷⁴ The sterically more demanding *tert*-butyl groups in **1-tBu** and **2-tBu** cause a distortion of the ring. The Zn–E–Sn angles are widened by 8° (E = S) or 5° (E = Se) compared to the methyl and phenyl derivatives; also, the distance between zinc and the tmeda ligands increases to avoid steric interactions with the *tert*-butyl groups. Bond lengths and angles of the {(tmeda)ZnS₂}²⁻ units are similar to those in the reported crystal structure of the intermediate [(tmeda)Zn(ESiMe₃)₂].⁷⁰ The Sn–E bond lengths of the chalcogen atom between the tin atoms are longer than of those bridging tin and zinc atoms.

Characterization of the Complexes by PXRD and NMR Spectroscopy. Complexes 1-R and 2-Ph crystallized phase pure as confirmed by X-ray powder diffraction (PXRD) whereas 2-tBu crystallized in at least two phases (Supporting Information, Figures S1-S5). Triclinic crystals of 2-tBu could be isolated which have the same composition as the described crystal structure. However, the quality of the crystals was too poor for a complete crystal structure analysis.⁷⁵ Obviously different orientations of the tert-butyl groups lead to different packing in the crystal structures. NMR spectra confirm composition and connectivity in solution for all complexes, although in solution all complexes decompose slowly under formation of ZnS or ZnSe and organotin species; however, after 1 week the original product is still the main compound. (tBu₂SnS)₂ and (tBu₂SnSe)₂ could be identified as decomposition products of 1-tBu and 2-tBu. 1-Ph decomposes under formation of $(PhSn)_4S_6$. Phenylstannanes are known for metathesis reactions by exchange of phenyl groups.⁷⁶ As



Figure 1. Molecular structures of 1-Ph (left) and 2-Ph (right). Atoms are drawn as 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Symmetry code ('): -x, y, 0.5 - z.

	1-Me	1-Ph	1-tBu	2-Ph	2- <i>t</i> Bu
Zn1-N1	213.5(3)	213.4(2)	216.7(3)	213.2(3)	218.6(3)
Zn1-N2		215.1(2)	217.6(3)		217.9(3)
Zn1-E2	227.7(1)	226.54(7)	224.85(8)	238.44(4)	236.38(5)
Zn1-E3		226.98(7)	226.19(8)		238.01(5)
Sn1-E2	236.8(1)	236.32(7)	236.78(7)	247.27(4)	249.53(4)
Sn1-E1	242.49(9)	241.35(7)	240.90(8)	253.23(4)	253.98(5)
Sn2-E1		241.48(7)	241.72(8)		254.16(5)
Sn2-E3		235.20(7)	238.17(8)		250.80(4)
N1-Zn1-N1'/N2	86.2(2)	85.79(9)	84.5(1)	85.3(2)	84.5(1)
E2-Zn1-E2'/E3	121.99(6)	126.86(3)	128.61(3)	126.49(3)	128.74(2)
E1-Sn1-E2	112.21(3)	115.13(2)	116.27(3)	118.53(1)	117.07(2)
E1-Sn2-E3		113.54(2)	118.67(3)		119.79(2)
Sn1-E1-Sn1'/Sn2	100.65(5)	103.10(3)	110.08(3)	98.85(2)	106.51(2)
Zn1-E2-Sn1	99.04(4)	98.87(2)	106.84(3)	99.44(2)	104.57(2)
Zn1-E3-Sn2		99.51(2)	107.10(3)		104.79(2)



Figure 2. ¹H, ¹¹⁹Sn{¹H}, and ⁷⁷Se{¹H} NMR spectra of 2-Ph in THF- d_8 .

Scheme 2. Proposed Thermolysis Reaction of a Mixture of 1-Me and $[(iPr_3PCu)_2(SC_2H_4S)]_2$ Forming CZTS and Volatile Thermolysis Products (Red)^{*a*}

 $[(tmeda)\text{Zn}(\text{SnMe}_2)_2\text{S}_3] + 0.5 [i\text{Pr}_3\text{PCu})_2(\text{SC}_2\text{H}_4\text{S})]_2 \xrightarrow{\Delta} \text{Cu}_2\text{Zn}\text{SnS}_4 + tmeda + 2 i\text{Pr}_3\text{P} + \text{C}_2\text{H}_4\text{S} + \text{SnMe}_4$

1-Me

10.4 % 28.7 % 5.4 % 16.0 %

^aThe percentage numbers correspond to the expected mass loss according to the given overall reaction equation.

representative examples, ¹H, ¹¹⁹Sn{¹H}, and ⁷⁷Se{¹H} NMR spectra of **2-Ph** in THF- d_8 are shown in Figure 2; NMR spectra of the other compounds are reported in the Supporting Information (Figures S6–S9).

The ¹H NMR spectrum of **2-Ph** shows two signals for the methylene and methyl protons of the tmeda ligand as well as two signal groups for the SnPh₂ ortho, meta, and para protons. The ortho-H atoms exhibit two satellite pairs resulting from ²J coupling to ¹¹⁷Sn and ¹¹⁹Sn nuclei. Consistent with the C_2 symmetry (crystallographic symmetry in **1-Me** and **2-Ph**) of the complex molecules, both tin atoms are chemically and magnetically identical and give one signal in the ¹¹⁹Sn{¹H} NMR spectrum at -65 ppm. The selenium atoms binding to two tin atoms and the selenium atom bridging tin and zinc atoms result in two signals in the ⁷⁷Se NMR spectrum at -433 ppm for Se1 and -531 ppm for Se2. The Sn–Se coupling constants are ¹J_{SnSe} = 1225 Hz for the longer Sn1–Se1 bonds and 1580 Hz for the shorter Sn1–Se2 bonds; the satellite pairs are well-separated in the ¹¹⁹Sn spectrum. Due to the magnetic

difference between ¹¹⁷Sn and ¹¹⁹Sn isotopes, ${}^{2}J_{SnSn}$ coupling is visible between ¹¹⁹Sn and the chemically identical, symmetry equivalent tin atom, if their two positions in the six-membered ring are occupied by one ¹¹⁷Sn and one ¹¹⁹Sn atom each.

Thermal Behavior and Thermolysis Studies. Complexes **1-R** and **2-R** are potential sources of Zn, Sn, and S or Se, respectively, in thermolysis reactions. Although their Zn/Sn ratio of 1/2 is different from that in the kesterite type semiconductors Cu_2ZnSnE_4 , cothermolysis reactions together with $[(iPr_3PCu)_2(EC_2H_4E)]_2$ as a Cu^I source were performed. Both phosphine stabilized copper ethane dichalcogenolate complexes thermally decompose under elimination of ethylene sulfide or ethene and selenium to form copper sulfide or copper selenide, respectively.^{53,54} Zinc tin complexes **1-R** and **2-R**, respectively, were homogeneously mixed with the copper sulfide/selenide source and thermally treated in a simultaneous thermogravimetric and difference thermoanalysis experiment (TG/DTA) up to 600 °C. An elimination of the tin excess during thermolysis is possible since exchange reactions during



Figure 3. Cothermolysis of a 2:1 mixture of 1-Me and $[(iPr_3PCu)_2(SC_2H_4S)]_2$ at temperatures up to 600 °C. The TG curve (black), the DTA curve (olive), and selected ion current curves are shown.



Figure 4. Rietveld refinement ($wR_p = 4.58\%$, $R_p = 3.50\%$, $R_{exp} = 2.86\%$) of the powder diffraction pattern ($\lambda = 154.060$ pm) obtained from the cothermolysis residue of **1-Me** with 0.5 equiv of $[(iPr_3PCu)_2(SC_2H_4S)]_2$ at temperatures up to 600 °C. Measured, calculated intensities, background curve, and difference curve as well as reflection positions of CZTS (78.2(7) wt %, first row), ZnS (8.4(2) wt %), SnS (2.7(1) wt %), tetragonal Cu₂S (1.9(2) wt %), and monoclinic Cu₂S (8.8(5) wt %).

the thermolysis can result in volatile tin compounds such as SnR_4 . The proposed reaction equation for the cothermolysis of a mixture of **1-Me** with 0.5 equiv of $[(iPr_3Cu)_2(SC_2H_4S)]_2$ is shown in Scheme 2; the results of the simultaneous thermal analysis are presented in Figure 3. Related thermal analysis results for mixtures of **1-Ph**, **1-tBu**, **2-Ph**, and **2-tBu** with $[(iPr_3Cu)_2(EC_2H_4E)]_2$ are shown in Figures S10–S13. All expected decomposition products besides CZTS are volatile and observed in the mass spectra of the volatile thermolysis products. Thermolysis studies of **1-R** and **2-R** without a copper source reveal decomposition at similar temperatures as in the cothermolysis products. The experimentally observed weight loss is significantly higher than expected for the

stoichiometric formation of zinc and tin chalcogenides. According to the weight loss for **1-Me** (observed, 52.4 wt %; calculated for the quantitative formation of ZnS and SnS, 30.7 wt %), volatile organotin compounds are formed; for **1-tBu** and **2-tBu**, *iso*-butene is detected by mass spectrometry (Figures S24–S26).

Thermolysis starts at 169 °C (onset temperature) with elimination of the tmeda and iPr_3P ligands: tmeda ($T_b = 120$ °C) is detected by the increase of the mass signal m/z = 58 ((CH₃)₂N = CH₂⁺); iPr_3P ($T_b = 170$ °C) is detected at m/z = 43 (iPr^+). The methyl groups of the SnMe₂ units are detected at m/z = 15 (CH₃⁺). Before the end of decomposition at 300 °C, the decomposition of ethane dithiolate forms ethylene sulfide (m/z = 60, $C_2H_4S^+$) and ethene (m/z = 28, $C_2H_4^+$). The

Article

Table 2. Details for Cothermolysis	Experiments of 1-R and 2-F	R Together with [(<i>i</i> Pr₃PC	$[u]_2(SC_2H_4S)]_2$ or
$[(i\Pr_3PCu)_2(SeC_2H_4Se)]_2^a$	-	-	

	1-Me	1-Ph	1-tBu	2-Ph	2- <i>t</i> Bu
		TG/	DTA		
start	80 °C	100 °C	100 °C	124 °C	100 °C
end	300 °C	350 °C	280 °C	340 °C	260 °C
calcd mass loss	60.5%	67.8%	65.7%	60.7%	58.7%
exp mass loss	63.6%	63.8%	65.3%	59.1%	49.7%
		PX	RD		
CZTSICZTSe	78.2(4) wt %	72.2(3) wt %	24.9(2) wt %	11.1(2) wt %	43.4(3) wt %
ZnSlZnSe	8.4(2) wt %	9.0(2) wt %	20.3(2) wt %	27.7(2) wt %	18.6(5) wt %
SnSlSnSe	2.7(1) wt %	3.8(1) wt %	28.7(2) wt %	32.1(2) wt %	11.2(2) wt %
Cu ₂ SlCu ₂ Se	10.7(5) wt %	15.0(3) wt %	26.1(2) wt %	29.1(2) wt %	12.4(2) wt %
Cu_2SnSe_4					14.5(6) wt %
Cu	26.7(5) mol %	28.3(3) mol %	25.3(2) mol %	24.0(4) mol %	24.2(5) mol %
Zn	14.4(2) mol %	14.0(2) mol %	15.2(2) mol %	17.1(2) mol %	15.4(4) mol %
Sn	10.7(1) mol %	10.3(1) mol %	14.2(1) mol %	14.2(2) mol %	11.8(3) mol %
S	48.2(6) mol %	47.4(4) mol %	45.3(6) mol %	44.7(5) mol %	48.6(9) mol %
'The Cu, Zn, Sn, and S	S percentages are calculat	ed from the results of pl	hase analysis by PXRD.		

experimental mass loss of 63.6% is 3.1% higher than expected. The reason is that more than 50% of the tin atoms, as expected in the idealized reaction equation in Scheme 2, are eliminated during thermolysis as volatile compounds.

In order to check the phase composition of the solid thermolysis residue, the X-ray powder diffraction pattern (Figure 4) has been analyzed. According to the Rietveld refinement of the diffraction pattern, 78.2 wt % CZTS, 8.4 wt % ZnS, 10.7 wt % Cu₂S, and 2.7 wt % SnS were formed. ZnS and Cu₂S were formed due to the loss of tin during thermolysis. SnS probably arises from the decomposition of CZTS under evolution of gaseous sulfur.⁷⁷ The molar percentages of copper, zinc, tin, and sulfur calculated on the basis of the phase composition data are in agreement with SEM-EDX analysis results of the thermolysis residue of 1-Me. EDX signal intensities measured in an area of 160 μ m \times 230 μ m correspond to 28 mol % copper, 16 mol % zinc, 11 mol % tin, and 45 mol % sulfur (Figure S23). Table 2 also summarizes the phase compositions after cothermolysis of 1-R and 2-R (R = Me, tBu) together with $[(iPr_3PCu)_2(EC_2H_4E)]_2$ as determined by Rietveld analysis (Figures S14-S17).

Thermolysis of 1-Ph with $[(iPr_3PCu)_2(SC_2H_4S)]_2$ needs a 50 K higher temperature compared to that for 1-Me due to the lower volatility of the phenylstannanes. Rietveld analysis (Figure S14) confirms the elimination of more than 50% of the tin atoms of 1-Ph. The yield of CZTS decreases to 72.2 wt %. The quantitative determination of CZTS and ZnS by PXRD is difficult since Cu_2SnS_3 could be formed as a side product. Cu_2SnS_3 crystallizes with lattice parameters almost identical to those of ZnS and very close to those of CZTS.

Thermolysis of **1-tBu** together with $[(iPr_3PCu)_2(SC_2H_4S)]_2$ results in 24.9 wt % CZTS. We assume a different thermolysis mechanism. While a radical cleavage is likely for the Sn–C bonds in **1-Me** and **1-Ph**, **1-tBu** can undergo β -hydride elimination under formation of *iso*-butene. *iso*-Butene was detected during thermolysis by the mass signals m/z = 56 $(C_4H_8^+)$ and 41 $(C_3H_5^+)$. The hydride ion is transferred to tin, and the reducing conditions favor the formation of SnS (28.7 wt %) in the thermolysis product. This alternative thermolysis mechanism also explains the lower thermolysis end temperature of 280 °C which is even lower than that of **1**. Thermolysis of **2-Ph** with $[(iPr_3PCu)_2(SeC_2H_4Se)]_2$ at temperatures up to 600 °C yields only 11.1 wt % CZTSe. Selenide ions are easily oxidized; thus, reduction of Sn^{IV} to Sn^{II}Se is preferred. Due to β -hydride elimination, the thermolysis of **2-tBu** is already complete at 260 °C. Under these conditions the reduction of Sn^{IV} is limited, and the content of CZTSe increases to 43.4(3) wt %. However, exact determination of the CZTSe content by analysis of the X-ray diffraction pattern is difficult since formation of other phases cannot be ruled out: Cu₂SnSe₄ crystallizes in cubic space group $F\overline{4}3m$ with lattice parameters very close to those of CZTSe. According to these results, both selenium complexes, **2-Ph** and **2-tBu**, together with $[(iPr_3PCu)_2(SeC_2H_4Se)]_2$ form Cu₂ZnSnSe₄, however, not as a pure product.

SUMMARY AND CONCLUSIONS

We successfully synthesized a series of five isostructural neutral zinc tin chalcogenide complexes $[(\text{tmeda})\text{Zn}(\text{SnR}_2)_2\text{E}_3]$ (R = Me, Ph, *t*Bu; E = S, Se). All complexes are characterized by X-ray single crystal structure analysis. They consist of sixmembered ZnSn_2E_3 rings in twist boat conformation; ¹H, ¹¹⁹Sn{¹H}, and ⁷⁷Se{¹H} NMR spectra confirm the presence of the molecular structures in solution. The molecular complexes **1-R** and **2-R** contain three out of four elements that are required for the formation of Cu₂ZnSnS₄ or Cu₂ZnSnSe₄. Although the formation of volatile tin compounds and reduction to Sn^{II} prevent quantitative formation of Cu₂ZnSnE₄ (E = S, Se) in cothermolysis experiments together with the copper chalcogenolate complex $[(iPr_3PCu)_2(\text{EC}_2H_4\text{E})]_2$, thermolysis yields are up to 78 wt % CZTS and 43 wt % CZTSe.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b01697.

Detailed information on analytical studies, including crystal structure data, X-ray powder diffraction patterns, and NMR spectra of 1-R and 2-R; thermogravimetric data of the cothermolyses of 1-R together with $[(iPr_3PCu)_2(SC_2H_4S)]_2$ and 2-R together with

 $[(iPr_3PCu)_2(SeC_2H_4Se)]_2$; X-ray powder diffraction patterns of the thermolysis products; temperature dependent X-ray powder diffraction patterns of the cothermolyses; SEM and EDX analysis; thermogravimetric data of 1-Me, 1-tBu, and 2-tBu (PDF)

Accession Codes

CCDC 1555378–1555382 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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DEDICATION

This work is dedicated to Prof. Dr. Dieter Fenske on the occasion of his 75th birthday.

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