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COMMUNICATION

Cyclic and polycyclic tellurium–tin and tellurium–lead compounds – synthesis, structures and thermal decomposition[†]

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The miscellaneously substituted silyItellanes $tBu_2PhSiTeSiMe_3$ (1) and $(Me_3Si)_3SiTeSiMe_3$ were used to synthesize the cyclic tin(II) and lead(II) tellurolates $[(tBu_2PhSiTe)_4M_2]$ (M = Sn (2), Pb (3)), $[tBu_2PhSiTePbC(SiMe_3)_3]_2$ (4) and the uncommon cluster compound $[{(Me_3Si)_3SiTe}_4Te_2Sn_4]$ (5).

Besides the fundamental interest in the formation and stability of chemical bonds between heavy main group elements, binary molecular compounds of the systems M-Te (M = Sn, Pb) are of considerable interest because of their potential use as singlesource precursors for the formation of MTe nanocrystals or thermoelectric materials.^{1,2} However, molecular compounds of these compositions are still scarce due to the high instability of bonds between these elements. Whereas several tellurium compounds of tin(IV) and lead(IV) such as $(R_2SnTe)_n$ (R = Me, Ph, n = 3; $\mathbf{R} = t\mathbf{Bu}$, $Fe(CO)_2Cp$, $Mo(CO)_3Cp$, n = 2) and $4-CH_3C_6H_4COTeMPh_3$ (M = Sn, Pb) are known,³ tellurium compounds of tin(II) and lead(II) are rarely described.^{4–8} Examples are the cyclic compounds $[M{TeSi(SiMe_3)_3}_2]_2$ or the ditellurido imidodiphosphinate complexes $[M{(TePiPr_2)_2N}_2]$ (M = Sn, Pb).^{1*a*,5} Furthermore, the chemistry of the anions $[PbTe_3]^{4-}$ and $[M_2Te_3]^{2-}$ (M = Sn, Pb) has been the focus of research for several years.⁶ Moreover, the 1D-phenyltellurolato complex [Sn(TePh)₂] is worth mentioning.7 Recently, mixed valence organo tin tellurides were described. These compounds were obtained from the reaction of the tin(I) species $(RSn)_2$ (R = pincer-type ligand) with elementary tellurium.8

Here, we report on our research on molecular compounds of the system M–Te (M = Sn, Pb) and describe the synthesis and crystal structure of the dimeric complexes $[(tBu_2PhSiTe)_4M_2]$ (M = Sn (2), Pb (3)), $[tBu_2PhSiTePbC(SiMe_3)_3]_2$ (4) and the uncommon cluster compound $[\{(Me_3Si)_3SiTe\}_4Te_2Sn_4]$ (5).

Organosilicon substituents with a high steric demand are good protecting groups in main group chemistry.⁹ For this reason, we synthesized the miscellaneously substituted silyltellane *t*Bu₂PhSiTeSiMe₃ (1) with the large *t*Bu₂PhSi group as a protecting group and a Me₃Si substituent as a leaving group.¹⁰ Compound 1 was obtained as a greenish oil in a yield of 91%. The ¹²⁵Te NMR spectrum shows a singlet at -998.3 ppm, and in the ²⁹Si{¹H}-NMR spectrum, two different signals at -5.6 ppm and at 30.9 ppm – each as a singlet – can be observed.

Based on the successful synthesis of binary bismuth–tellurium species in the reactions of the miscellaneously substituted silyltellane with chlorobismuthanes,¹¹ we investigate reactions of silyltellanes **1** and (Me₃Si)₃SiTeSiMe₃¹² with metal salts of Sn and Pb.

The reaction of **1** with SnCl₂ in Et₂O at -74 °C leads to a yellow solution. From this solution, $[(tBu_2PhSiTe)_4Sn_2]$ (**2**) can be obtained as yellow crystals in a good yield. Compound **2** crystallizes in the monoclinic spacegroup $P2_1/c$ with four molecules in the unit cell (Fig. 1). The molecular structure can be described as a dimer of two $(tBu_2PhSiTe)_2Sn$ fragments under formation of a folded four-membered ring with an angle of torsion along the Te(1)–Te(2) axis of 137.7°. The substituents around the ring show an all-*trans* arrangement. The Sn–Te bond lengths in the Sn₂Te₂ core are between 293.9(2) pm and 299.0(2) pm and in the same range as the endocyclic bonds



Fig. 1 Molecular structure of **2**; thermal ellipsoids represent a 50% probability level, hydrogen atoms are not shown, selected bond lengths (pm) and angles ($^{\circ}$): Sn(1)–Te(1) 299.0(2), Sn(1)–Te(2) 293.9(2), Sn(2)–Te(1) 295.6(2), Sn(2)–Te(2) 297.5(2), Sn(1)–Te(4) 281.8(2), Sn(2)–Te(3) 283.3(2), Te(1)–Si(1) 254.5(6), Te(2)–Si(2) 254.3(7), Te(3)–Si(3) 251.3(5), Te(4)–Si(4) 252.5(5); Sn(1)–Te(1)–Sn(2) 81.67(6), Sn(1)–Te(2)–Sn(2) 90.26(6), Te(1)–Sn(1)–Te(2) 81.48(5), Te(1)–Sn(2)–Te(2) 81.46(6), Te(1)–Sn(1)–Te(4) 93.46(7), Te(1)–Sn(2)–Te(3) 87.90(6), Te(2)–Sn(1)–Te(4) 89.06(6), Sn(2)–Te(3) 90.53(6), Sn(2)–Te(3)–Si(3) 102.21(16), Sn(1)–Te(4)–Si(4) 104.38(15), Sn(1)–Te(1)–Te(2)–Sn(2) 137.71(8).

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in $[{(Me_3Si)_3SiTe}_2Sn]_2$ (294.6 pm–295.6 pm).⁵ In contrast, the exocyclic Sn–Te bonds are shortened due to the lower coordination number of these Te atoms (281.8(2) pm and 283.3(2) pm).

Room-temperature NMR experiments do not show the expected signals for the cyclic and the exocyclic silyltellurolato ligand. Instead, the ¹H NMR spectrum shows one peak for the *tert*-butyl groups and just one set of phenyl signals. The ¹²⁵Te NMR spectrum displays only one singlet at -715.0 ppm. The ²⁹Si{¹H} NMR spectrum shows one singlet at 34.7 ppm. Low-temperature ¹H NMR experiments exhibit coalescence at -3 °C and suggest a displacement of the *t*Bu₂PhSi groups in solution. A complete splitting of the *t*Bu group signals with a value of 76 Hz can be achieved at -70 °C and leads to an energy barrier $\Delta G^{\ddagger} = 54.3$ kJ mol⁻¹.

We also succeeded in synthesizing a lead–tellurium compound, by the reaction of **1** with PbCl₂ in Et₂O at -74 °C. Orange crystals of the cyclic species [(*t*Bu₂PhSiTe)₄Pb₂] (**3**) form during a period of two days. Compound **3** crystallizes in the monoclinic space group *C*2/*c* with four molecules in the unit cell (Fig. 2). The molecular structure is almost identical to that of tin compound **2**. The angle of torsion is 138.4° and in the same range as in the tin compound. The Pb–Te bond lengths in the Pb₂Te₂ core are between 300.0(1) pm and 303.8(1) pm, whereas the exocyclic bonds with 289.2(1) pm are somewhat shorter. Therefore, the measured Pb–Te bond lengths are in the same range as in the [Pb₂Te₃]^{2–} anion (295.9 pm–301.5 pm),^{6e} but considerably longer than the sum of the calculated covalent radii (280 pm).¹³

NMR analysis of **3** shows signals which indicate the existence of only one $tBu_2PhSiTe$ group. Low-temperature NMR experiments do not display the expected coalescence, instead signals that suggest a monomer–dimer equilibrium. This may be a consequence of the less stable Pb–Te bonds in comparison to the Sn–Te bond of compound **2**.¹⁴

 $[tBu_2PhSiTePbC(SiMe_3)_3]_2$ (4) was obtained from the reaction of 1 with the tris(trimethylsilyl)methylchloridoplumbylene (Me_3Si)_3CPbCl in Et_2O (Fig. 3).¹⁵ It crystallizes as red blocks upon cooling the reaction mixture to -35 °C. The structure solution and refinement were carried out in the monoclinic space group $P2_1/n$ with four molecules in the unit cell. The



Fig. 2 Molecular structure of **3**; thermal ellipsoids represent a 50% probability level, hydrogen atoms are not shown, selected bond lengths (pm) and angles (°): Pb(1)–Te(1) 303.8(1), Pb(1)–Te(1)' 300.0(1), Pb(1)–Te(2) 289.2(1), Te(1)–Si(1) 254.7(1), Te(2)–Si(2) 251.6(2); Te(1)–Pb(1)–Te(1)' 81.65(3), Te(1)–Pb(1)–Te(2) 91.34(2), Te(1)'–Pb(1)–Te(2) 88.29(1), Pb(1)–Te(1)–Pb(1)' 100.3(3), Si(1)–Te(1)–Pb(1) 110.68(3), Si(1)–Te(1)–Pb(1)' 104.63(4), Si(2)–Te(2)–Pb(1) 102.34(4); Pb(1)–Te(1)–Te(1)'–Pb(2) 138.36(3).



Fig. 3 Molecular structure of **4**; thermal ellipsoids represent a 50% probability level, hydrogen atoms are not shown, selected bond lengths (pm) and angles (°): Pb(1)–Te(1) 310.4(1), Pb(1)–Te(2) 313.2(1), Pb(2)–Te(1) 313.7(1), Pb(2)–Te(2) 306.9(1), Te(1)–Si(1) 257.3(4), Te(2)–Si(2) 257.9(3), Pb–C 241.4(11)–244.7(13); Te(1)–Pb(1)–Te(2) 83.60(3), Te(1)–Pb(2)–Te(2) 84.09(3), Pb(1)–Te(1)–Pb(2) 92.06(3), Pb(1)–Te(2)–Pb(2) 92.84(3); Pb(1)–Te(1)–Te(2)–Pb(2) 152.1(3).

molecular structure consists of a Pb_2Te_2 core folded slightly in a butterfly manner with an angle of torsion of 152.1° along the Te(1)–Te(2) axis. The organosilicon ligands at the Pb and Te atoms are all *trans*-aligned. The Pb–Te bond distances are between 306.9(1) pm and 313.2(1) pm and hence considerably longer than the lengths of core Pb–Te bond in **3**. This may be a result of the steric demand of the organosilicon ligands at the lead and the tellurium atoms.

Starting from $(Me_3Si)_3SiTeSiMe_3^{12}$ and $SnCl_2$ at a molar ratio of 1 : 1, we obtained the unique cluster $[{(Me_3Si)_3SiTe}_{4}-$ Te₂Sn₄] (5), which can be isolated as dark red crystals upon cooling the reaction mixture to -35 °C (Fig. 4). Compound 5 crystallizes in the monoclinic space group $P2_1/n$ with two molecules in the unit cell and consists of a Te₆Sn₄-framework with four peripheral (Me₃Si)₃Si groups. The structure can be described as a planar Sn₂Te₂ ring with two exocyclic {(Me₃Si)₃SiTe}₂Sn fragments, which are trans-aligned to each other. Surprisingly, the molecules contain two Te²⁻ ions beside four (Me₃Si)₃SiTe⁻ ligands. This shows that the (Me₃Si)₃Si substituent can act as a leaving group under these conditions.

Within the central Te₂Sn₂ ring the Sn(2)–Te(3)–Sn(2)' bond angle amounts to 89.29(1)°, the Te(3)–Sn(2)–Te(3)' bond angle to 90.71(1)°. The Te–Sn bonds within the Te₂Sn₂ ring are 290.3(1) and 292.6(1) pm long and therefore shorter than in compound **2**. The exocyclic Sn–Te bonds around Sn(1) show values of 286.2(2) pm (Sn(1)–Te(1)), 288.6(1) pm (Sn(1)–Te(2)) and 296.1(1) pm (Sn(1)–Te(3)). Besides these covalent bonds, secondary interactions between Te(1) and Sn(2) (330.4(8) pm) as well as Te(2) and Sn(2)' (313.6(8) pm) can be observed which are between covalent bonds and van der Waals interactions (423.0 pm).^{13,16}

Furthermore, the Te_6Sn_4 core of compound **5** displays a fragment of the cubic SnTe. Therefore, this compound represents an intermediate stage of the formation of the binary SnTe phase from the molecular precursor [Sn{TeSi(SiMe_3)_3}_2]_2 as described by Seligson and Arnold.⁵

Thermogravimetric analysis under helium gas flow was carried out for compounds 2–5. Compound 2 decomposes in the



Fig. 4 Molecular structure of 5; thermal ellipsoids represent a 50% probability level, hydrogen atoms are not shown, selected bond lengths (pm) and angles (°): Sn(1)–Te(1) 286.2(2), Sn(1)–Te(2) 288.6(1), Sn(1)–Te(3) 296.1(1), Sn(2)–Te(3) 290.3(1), Sn(2)–Te(3)' 292.6(1), Te(2)–Sn(2)' 313.6(8), Te(1)–Sn(2) 330.4(8), Te(1)–Si(1) 253.5(2), Te(2)–Si(5) 235.9(2); Te(1)–Sn(1)–Te(2) 83.72(2), Te(1)–Sn(1)–Te(3) 96.52(3), Te(2)–Sn(1)–Te(3) 94.96(2), Sn(1)–Te(3)–Sn(2) 90.10(3), Sn(1)–Te(3)–Sn(2)' 87.62(2), Te(3)–Sn(2)–Te(3)' 90.71(2), Sn(2)–Te(3)' Sn(2)(89.29(1).

temperature range of 210-290 °C with an overall mass loss of 66.7% (calculated for the formation of SnTe: 69.7%). A different behaviour was observed for compound 3, which shows a first decomposition step between 50 and 75°C with a mass loss of 11.9%. This corresponds to the elimination of one tBu₂PhSi group (calc. 12.2%). Further decomposition occurs in the temperature range of 190 to 250 °C with a mass loss of 51.93% and indicates the formation of PbTe. Compound 4 shows a gradual mass loss in the temperature range of 100 to 300 °C with a shoulder at 190 °C. The overall mass loss is 55.1%, which fits roughly to the formation of PbTe (calc. 57.4%). Finally, the thermal decomposition of cluster compound 5 was investigated. However, in all experiments under helium gas flow as well as under vacuum, 5 shows a mass loss much larger than expected for the formation of SnTe: calc. 55.8%, observed under helium gas flow 61.8% and 71.2% under vacuum.

Organosilicon tellanes are possible precursors to obtain telluro-bridged compounds of tin and lead. The uncommon multinuclear complex **5** can be described as part of the cubic SnTe and gives insight into the formation of solid states from molecular precursors. Apart from the Sn–Te system with compounds **3** and **4**, we succeeded in synthesizing and structurally characterizing two stable compounds containing lead–tellurium bonds. Moreover, such compounds are promising single source precursors for SnTe and PbTe as thermoelectric materials.

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