Cyclic and polycyclic tellurium tin and tellurium lead compounds – species between molecules and the solid phase**

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Supplementary information

Experimental Details

All manipulations were performed under rigorous exclusion of oxygen and moisture using a Schlenk line and argon atmosphere. Solvents were dried and freshly distilled before use. The starting materials were prepared according to literature: *t*Bu_2PhSiTeNa(thf)$_2$,[i] $(Me_3Si)_3SiTeSiMe_3$[ii] and $(Me_3Si)_3CPbCl$[iii]. NMR spectra were recorded using a "*Bruker Avance III* (500 MHz)" spectrometer and were referenced internally to the deuterated solvent. C_6D_6 was dried over Na/benzophenone. EI-MS spectra were recorded on a "*Varian MAT 3830* (70 eV)".

tBu_2PhSiTeSiMe$_3$ (1):

At room temperature, Me_3SiCl (14.1 mmol; 1.8 ml) was added to a suspension of *t*Bu_2PhSiTeNa(thf)$_2$ (8.28 mmol; 4.26 g) in 200 ml *n*heptane. After stirring for additional 16 h, the solvent was removed under vacuum. The residue was suspended in 50 ml *n*pentane, and the precipitated NaCl was subsequently removed by centrifugation. After removal of the solvent, **1** was obtained as green oil (3.18 g; 91%). ^{1}H NMR (C_6D_6): δ = 0.35 [s, Si*C*H$_3$, 9H], 1.26 [s, C(*C*H$_3$)$_3$, 18H], 7.06-7.11 [m, ortho + para Ph, 3H], 7.94-7.97 [m, meta Ph, 2H]; ^{13}C{^{1}H} NMR (C_6D_6): δ = 5.6 [s, Si*C*H$_3$], 22.8 [s, *C*(CH$_3$)], 30.3 [s, *C*H$_3$], 127.7 [s, Ph], 129.6 [s, Ph], 134.8 [s, Ph], 137.7 [s, Ph]; ^{29}Si{^{1}H} NMR (C_6D_6): δ = -5.6 [s, *Si*Me$_3$], 30.9 [s, *Sit*Bu_2Ph]; ^{125}Te NMR (C_6D_6): -998.3 [s]; MS (EI, 70 eV) m/z (%): 348.8 [M^+ - $SiMe_3$] (8), 73.1 [$SiMe_3^+$] (100); IR (KBr): v = 484 (vs), 574 (s), 622 (s), 701 (s), 737 (s), 751 (m), 814 (vs), 840 (vs), 935 (m), 1010 (s), 1097 (vs), 1193 (m), 1247 (vs), 1364 (s), 1388 (s), 1427 (vs), 1471 (vs), 1820 (vw), 1888 (vw), 1956 (vw), 2859 (vs), 2888 (vs), 2953 (vs), 3046 (m), 3068 (m).

[(*t*Bu$_2$PhSiTe)$_4$Sn$_2$] (2):

A solution of *t*Bu$_2$PhSiTeSiMe$_3$ (1 mmol; 3.3 ml; 0.3 M in Et$_2$O) was added to a solution of SnCl$_2$ (0.5 mmol; 0.095 g) in 15 ml Et$_2$O at -74°C. The yellow solution was allowed to warm up to room temperature and was stirred for additional 30 min. The solvent was removed under vacuum, and the residual solid was dissolved in 5 ml of toluene. After 2 days, yellow rods could be obtained at -35°C. Yield: 162 mg (40%). Elemental analysis: calc. for $Te_4Sn_2Si_4C_{56}H_{92}$: C 41.38%, H 5.70%; found: C 41.36%, H 5.80%. ^{1}H NMR (C_6D_6): δ = 1.29 [s, C*H*$_3$, 18H], 7.11 [t, para Ph, $^{3}J_{H,H}$ = 7.2 Hz, 1H], 7.17 [t, meta Ph, $^{3}J_{H,H}$ = 7.2 Hz, 2H], 8.01 [d, ortho Ph, $^{3}J_{H,H}$ = 7.2 Hz, 2H]; ^{13}C{^{1}H} NMR (C_6D_6): δ =23.9 [s, *C*(CH$_3$)$_3$], 30.6 [s, C(*C*H$_3$)$_3$], 128.3 [s, Ph], 129.4 [s, Ph], 136.2 [s, Ph], 137.3 [s, Ph]; ^{29}Si{^{1}H} NMR (C_6D_6): δ = 34.7 [s]; ^{125}Te{^{1}H} NMR (C_6D_6): δ = -715.0 [s]; IR (KBr): ν = 455 (s), 470 (vs), 484 (vs), 573 (m), 614 (m), 700 (s), 741 (m), 816 (s), 933 (w), 1010 (m), 1095 (vs), 1176 (w), 1195 (w), 1262 (w), 1363 (w), 1384 (w), 1425 (s), 1468 (m), 1816 (vw, Ph), 1882 (vw, Ph), 1950 (vw, Ph), 2855 (s), 2888 (m), 2928 (vs), 2964 (s), 3068 (w).

[(*t*Bu$_2$PhSiTe)$_4$Pb$_2$] (3):

A solution of *t*Bu$_2$PhSiTeSiMe$_3$ (1 mmol; 3.3 ml; 0.3 M in Et$_2$O) was added to a suspension of PbCl$_2$ (0.5 mmol; 0.139 g) in 15 ml Et$_2$O at -74°C. The yellow solution was allowed to warm up to room temperature and was stirred for additional 30 min. The solvent was concentrated to 6 ml, and after 2 days, orange rods could be obtained at -35°C. Yield: 85 mg (19%). Elemental analysis: calc. for $Te_4Pb_2Si_4C_{56}H_{92}$: C 37.32%, H 5.14%; found: C 37.71%, H 5.56%. ^{1}H NMR (C_6D_6): δ = 1.26 [s, C*H*$_3$, 18H], 7.12 [t, para Ph, $^{3}J_{H,H}$ = 7.2 Hz, 1H], 7.20 [t, meta Ph, $^{3}J_{H,H}$ = 7.2 Hz, 2H], 8.00 [d, ortho Ph, $^{3}J_{H,H}$ = 7.2 Hz, 2H]; ^{13}C{^{1}H} NMR (C_6D_6): δ =23.9 [s, *C*(CH$_3$)$_3$], 30.6 [s, C(*C*H$_3$)$_3$], 128.3 [s, Ph], 129.4 [s, Ph], 136.1 [s, Ph], 137.2 [s, Ph]; ^{29}Si{^{1}H} NMR (C_6D_6): δ = 25.7 [s]; IR (KBr): ν = 456 (s), 473 (vs), 572 (m), 613 (m), 701 (s), 740 (m), 815 (vs), 1010 (s), 1094 (vs), 1262 (s), 1362 (m), 1385 (m), 1426 (s), 1468 (m), 1887 (vw), 1953 (vw), 2031 (vw), 2342 (w), 2856 (s), 2884 (m), 2929 (s), 3071 (w).

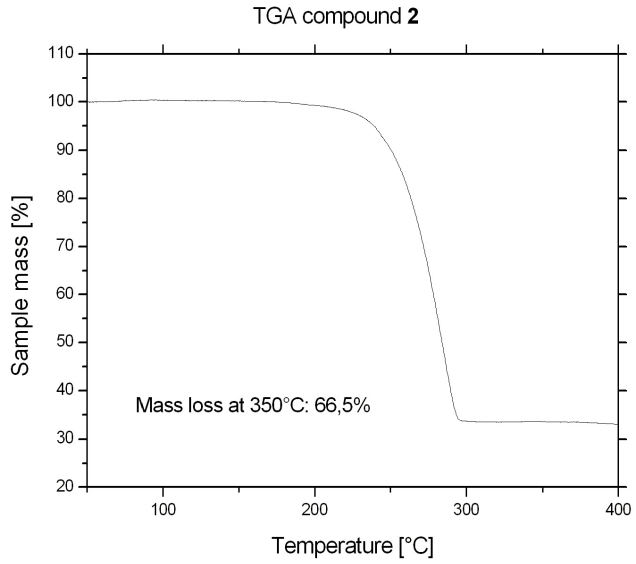
[*t*Bu$_2$PhSiTePbC(SiMe$_3$)$_3$]$_2$ (4):

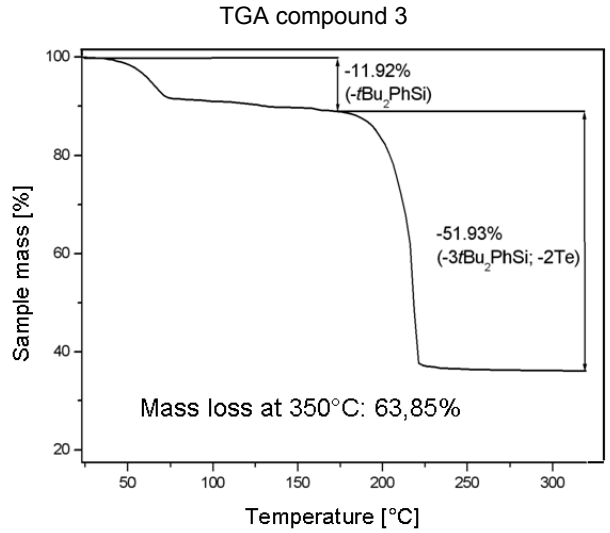
A solution of *t*Bu$_2$PhSiTeSiMe$_3$ (0.8 mmol; 3.0 ml; 0.3 M in Et$_2$O) was added to a suspension of (Me$_3$Si)$_3$CPbCl (0.8 mmol; 0.379 g) in 15 ml Et$_2$O at -74°C. The red solution was allowed to warm up to room temperature and was stirred for additional 30 min. The dark precipitate was removed by filtration, and the solvent was concentrated to 6ml. At -35°C, red rods of **4** were obtained. Yield: 301 mg (48%). Elemental analysis: calc. for $Te_2Pb_2Si_8C_{48}H_{100}$: C 36.68%, H 6.41%; found: C 36.98%, H 6.13%. Because of the instability of compound **4** in solution no satisfying NMR spectra could be obtained. IR (KBr): v = 453 (m), 481 (s), 542 (m), 572 (m), 614 (m), 647 (m), 672 (m), 701 (m), 736 (m), 856 (vs), 1008 (m), 1096 (m), 1251 (m), 1362 (w), 1386 (w), 1426 (w), 1492 (w), 2856 (m), 2890 (m), 2931 (m), 3070(vw).

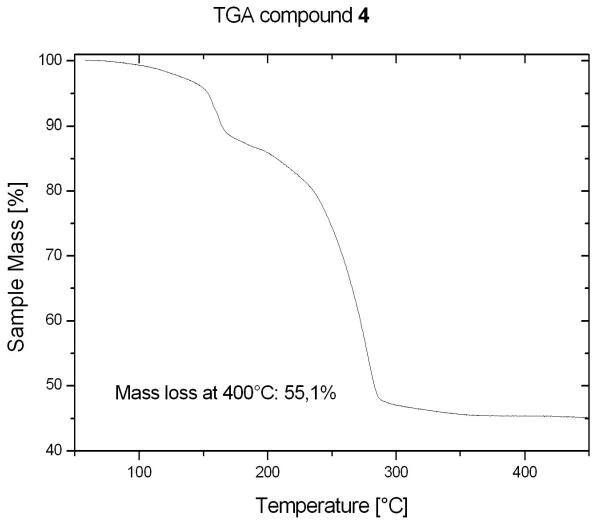
[{(Me$_3$Si)$_3$SiTe}$_4$Te$_2$Sn$_4$] (5):

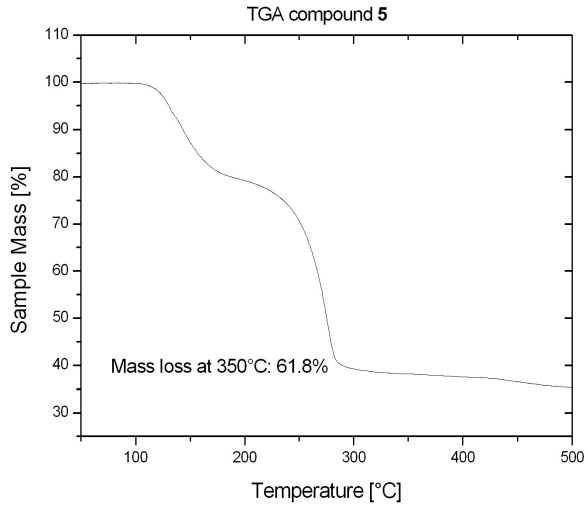
A solution of (Me$_3$Si)$_3$SiTeSiMe$_3$ (1 mmol; 5 ml; 0.2 M in Et$_2$O) was added to a solution of SnCl$_2$ (0.5 mmol; 0.095 g) in 10 ml Et$_2$O at -74°C. The yellow solution was allowed to warm up to room temperature and was stirred for additional 30 min. The solvent was concentrated to 4 ml, and after 5 days, red crystals could be obtained at -35°C. Yield: 70 mg (19%). Elemental analysis: calc. for $Te_6Sn_4Si_{16}C_{36}H_{108}$: C 19.38%, H 4.88%; found C 19.37%, H 4.89%. ^{1}H NMR (C_6D_6): δ = 0.42 [s, C*H*$_3$, 27H]; ^{13}C{^{1}H} NMR (C_6D_6): δ = 2.47 [s]; ^{29}Si{^{1}H} NMR (C_6D_6): δ = -92.3 [s, broad], -9.6 [s]; MS (EI, 70 eV) m/z (%): 750.1 [*hyp*$_2$Te$_2^+$] (13), 375.1 [*hyp*Te$^+$] (100), 303.1 [*hyp*Te$^+$ - Me] (23), 73 [Me$_3$Si$^+$] (100); IR (KBr): v = 621 (m), 689 (m) 834 (vs), 856 (m) 1019 (w), 1098 (w), 1243 (m), 1258 (w), 1393 (w), 2885 (w), 2946 (m).

Thermogravimetric analysis under helium gas flow

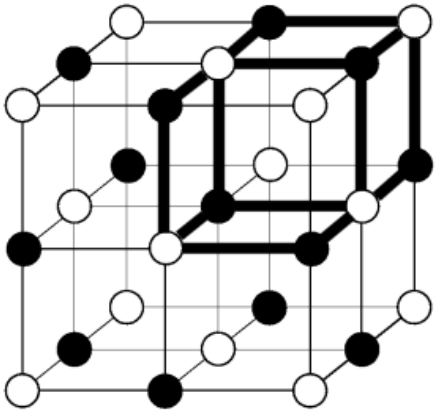






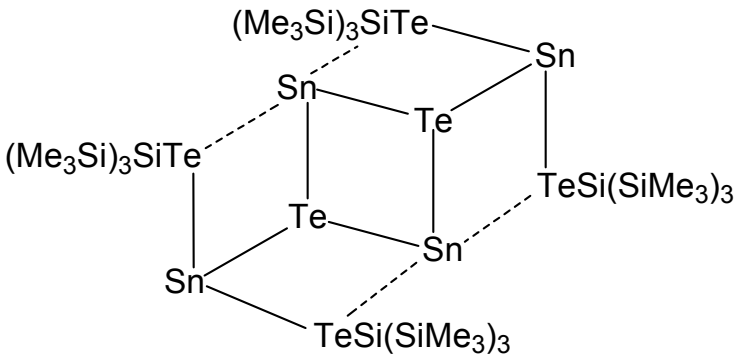


Compounds 5 (right) in comparison with the unit cell of cubic SnTe (left)



● = Te

○ = Sn



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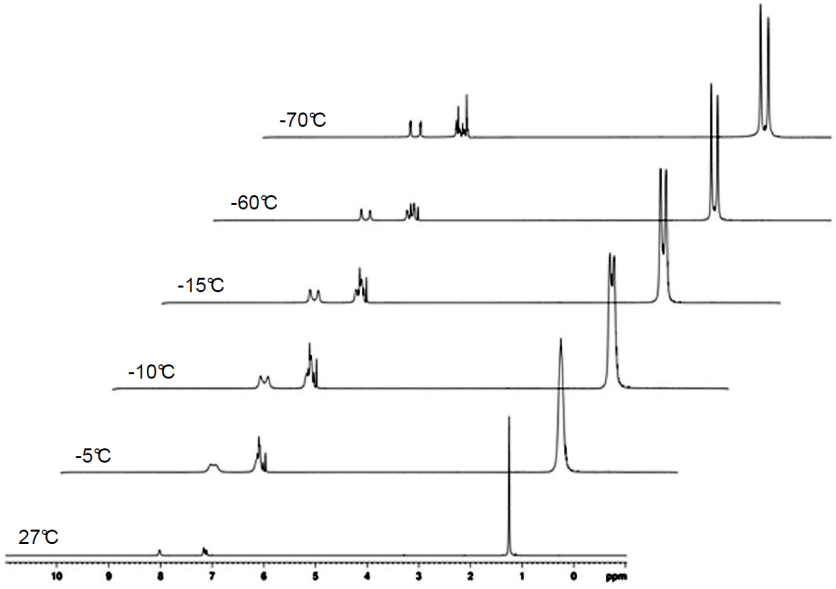
Temperature dependent ^{1}H NMR investigations of compound 2



X-ray data of the compounds 2-5

Compound 2:

Empirical formula	C56 H92 Si4 Sn2 Te4
Formula weight	1625.44
Temperature	180(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 29.684(3) Å alpha = 90 deg. b = 8.3463(5) Å beta = 118.768(6) deg. c = 30.084(3) Å gamma = 90 deg.
Volume	6533.5(9) $Å^3$
Z, Calculated density	4, 1.652 g/m^3
Absorption coefficient	2.620 mm^{-1}
F(000)	3168
Crystal size	0.449 x 0.029 x 0.024 mm
Theta range for data collection	1.54 to 22.73 deg.
Limiting indices	-32<=h<=31, -9<=k<=8, -32<=l<=32
Reflections collected / unique	24640 / 8634 [R(int) = 0.1726]
Completeness to theta = 22.73	98.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6244 and 0.5677
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8634 / 96 / 595
Goodness-of-fit on F^2	0.815
Final R indices [I>2sigma(I)]	R1 = 0.0716, wR2 = 0.0895
R indices (all data)	R1 = 0.1948, wR2 = 0.1230
Largest diff. peak and hole	0.665 and -0.731 $e·Å^{-3}$

Compound 3

Empirical formula	$C_{56}H_{92}Pb_2Si_4Te_4$
Formula weight	1802.44
Temperature	180(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 25.621(7) Å alpha = 90 deg. b = 8.1720(16) Å beta = 90.06(3) deg. c = 31.760(6) Å gamma = 90 deg.
Volume	6650(3) $Å^3$
Z, Calculated density	4, 1.800 g/cm^3
Absorption coefficient	6.880 mm^{-1}
F(000)	3424
Crystal size	0.4520 x 0.1180 x 0.0420 mm
Theta range for data collection	1.28 to 25.63 deg.
Limiting indices	-31<=h<=30, -9<=k<=6, -38<=l<=36
Reflections collected / unique	14149 / 5785 [R(int) = 0.0503]
Completeness to theta = 25.63	92.1 %
Absorption correction	Integration
Max. and min. transmission	0.7080 and 0.1960
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5785 / 0 / 310
Goodness-of-fit on F^2	0.974
Final R indices [I>2sigma(I)]	R1 = 0.0275, wR2 = 0.0673
R indices (all data)	R1 = 0.0344, wR2 = 0.0694
Largest diff. peak and hole	0.610 and -1.652 $e·Å^{-3}$

Compound 4

Empirical formula	$C_{48}H_{100}Pb_2Si_8Te_2$
Formula weight	1571.58
Temperature	180(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 13.762(6) Å alpha = 90 deg. b = 19.778(7) Å beta = 103.36(4) deg. c = 25.104(13) Å gamma = 90 deg.
Volume	6648(5) $Å^3$
Z, Calculated density	4, 1.570 g/cm^3
Absorption coefficient	6.090 mm^{-1}
F(000)	3072
Crystal size	0.1430 x 0.1230 x 0.0350 mm
Theta range for data collection	1.32 to 26.79 deg.
Limiting indices	-17<=h<=17, -24<=k<=24, -27<=l<=31
Reflections collected / unique	41516 / 14056 [R(int) = 0.0931]
Completeness to theta = 26.79	99.0 %
Absorption correction	Integration
Max. and min. transmission	0.8502 and 0.4408
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14056 / 0 / 573
Goodness-of-fit on F^2	0.953
Final R indices [I>2sigma(I)]	R1 = 0.0689, wR2 = 0.1458
R indices (all data)	R1 = 0.1312, wR2 = 0.1732
Largest diff. peak and hole	2.439 and -2.438 $e·Å^{-3}$

Compound 5

Empirical formula	$C_{36}H_{108}Si_{16}Sn_4Te_6$
Formula weight	2231.02
Temperature	180(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 9.5474(19) Å alpha = 90 deg. b = 26.049(5) Å beta = 91.70(3) deg. c = 17.285(4) Å gamma = 90 deg.
Volume	4297.0(15) $Å^3$
Z, Calculated density	2, 1.724 g/cm^3
Absorption coefficient	3.390 mm^{-1}
F(000)	2120
Crystal size	0.281 x 0.092 x 0.030 mm
Theta range for data collection	2.41 to 25.62 deg.
Limiting indices	-10<=h<=11, -31<=k<=31, -20<=l<=17
Reflections collected / unique	19869 / 7752 [R(int) = 0.0696]
Completeness to theta = 25.62	95.6 %
Absorption correction	Integration
Max. and min. transmission	0.9040 and 0.6503
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7752 / 0 / 280
Goodness-of-fit on F^2	1.052
Final R indices [I>2sigma(I)]	R1 = 0.0411, wR2 = 0.0939
R indices (all data)	R1 = 0.0540, wR2 = 0.0988
Largest diff. peak and hole	0.780 and -1.328 $e·Å^{-3}$

[i] T. Kückmann, M. Hermsen, M. Bolte, M. Wagner, H.-W. Lerner, *Inorg. Chem.*, **2005**, *44*, 3449-3458.
[ii] P. Bonasia, D. Gindelbert, B. Dabbousi, J. Arnold, *J. Am. Chem. Soc.*, **1992**, *114*, 5209-5214.
[iii] C. Eaborn, P. B. Hitchcock, J. D. Smith, S. E. Sözerli, *Organometallics,* **1997**, *16*, 5653-5658.