

***In-situ* Ge–Ge bond formation under ambient conditions: synthesis,
characterization and reactivity of organo-functionalized
telluridogermanate complexes**

Samuel Heimann Małgorzata Holyńska and Stefanie Dehnen

*Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse, 35043 Marburg,
Germany. E-mail: dehnen@chemie.uni-marburg.de; Fax: 49 6421 2825653; Tel: 49 6421 2825751*

SUPPORTING INFORMATION

1 Quantum chemical investigation

1.1 Methods of the quantum chemical investigations

DFT [S1] investigations were undertaken by means of the program system TURBOMOLE, version 5.10 [S2] using the RIDFT program [S3] with the Becke-Perdew 86 (BP86) functional [S4] and the grid size m3. Basis sets were of def2-TZVP quality (TZVP = triple zeta valence plus polarization) [S5]. The simultaneous optimizations of geometric and electronic structures were performed without symmetry restrictions, *i.e.* in C_1 symmetry, allowing for convergence into local minima at higher symmetry.

1.2 Calculation of reaction energies

The reaction energies of the non-isodesmic reactions (two T–E bonds on the reactant side versus one Ge–Ge bond on the product side) were calculated considering once the atomic energy of the released E atom (E_E), and once the energy of a T–E bond (E_{T-E}),^{1,2} thus according to the following reaction schemes and equations³



$$\Delta E_{DD-AD} = E_{DD} - E_{AD} \quad \text{eq. (4)}$$

$$\Delta E_{NA-DD} = [E_{NA} + E_E + E_{T-E}] - E_{DD} \quad \text{eq. (5)}^1$$

$$\Delta E_{NA-AD} = [E_{NA} + E_E + E_{T-E}] - E_{AD} \quad \text{eq. (6)}^1$$

Table S1. Total energies E for compounds $[(R^xT)_4E_6]^{DD}$, $[(R^xT)_4E_6]^{AD}$ and $[(R^xT)E_5]$ as resulting from DFT calculations for all combinations of tetrrels T = Ge, Sn and chalcogens E = S, Se, Te with organic ligands $R^x = R^1$ or R^2 . All values are given in Hartree (1 H = 2625.47 kJ·mol⁻¹).

T/E	R ¹ = CMe ₂ CH ₂ COMe			R ² = CH ₂ CH ₂ COOH		
	E _{AD}	E _{DD}	E _{NA}	E _{AD}	E _{DD}	E _{NA}
Ge/S	-11941,5242	-11941,5316	-11543,2382	-11770.76082	-11770.7697	-11372.486
Ge/Se	-23963,1011	-23963,1054	-21561,2172	-23792.33742	-23792.3438	-21390.4665
Ge/Te	-11161,0566	-11161,0572	-10892,8433	-10990.29289	-10990.2969	-10722.0945
Sn/S	-4490,12913	-4490,1201	-4091,82992	-4319.357287	-4319.36094	-3921.07176
Sn/Se	-16511,7285	-16511,718	-14109,8299	-16340.95666	-16340.9583	-13939.0718
Sn/Te	-3709,7034	-3709,69234	-3441,47631	-3538.932795	-3538.9336	-3270.7194

Table S2. Total energies E for E atoms and for compounds H_2E (E = S, Se, Te) as resulting from DFT calculations for. All values are given in Hartree (1 H = 2625.47 kJ·mol⁻¹).

species	E = S	E = Se	E = Te
E atom	-398.1595389234	-2401.776344641	-268.1291368368
H ₂ E	-399.4554774414	-2403.042830428	-269.3629512669

Energies of the T–E bonds (E_{T-E}),¹ reaction energies for the isomerization of AD isomers to DD isomers according to equations 1 and 4 (ΔE_{DD-AD}), and reaction energies for the reaction of DD isomers to NA-type clusters (ΔE_{NA-DD} , eqs. (2) and (5)) or reaction of AD-type isomers to NA-type clusters (ΔE_{NA-AD} , eqs. (3) and (6)), respectively, as resulting from DFT calculations for all combinations of tetrrels T = Ge, Sn and chalcogens E = S, Se, Te with organic ligands $R^x = R^1$ or R^2 in the *reactions* schemes eqs (1) – (3) are given in Table 1 in the main document.

Table S3. Overview of the experimentally observed structures for all combinations of tetrrels T = Ge, Sn and chalcogens E = S, Se, Te, and organic ligands $R^x = R^1$ or R^2 in compounds $[(R^xT)_4E_6]$ or $[(R^xT)E_5]$. Combinations highlighted by *italic* letter do not have any precedence so far.

T/E	$R^1 = CMe_2CH_2COMe$			$R^2 = CH_2CH_2COOH$		
	AD	DD	NA	AD	DD	NA
Ge/S						
Ge/Se						
Ge/Te						
Sn/S						
<i>Sn/Se</i>						
<i>Sn/Te</i>						

¹ The reactions, as given in Eqs. 1-3, are non-isodesmic, since two T–E bonds in the reactant are replaced by one T–T bond in the product. Since we are interested in the intrinsic difference of the stabilities of the complexes on both sides of the reactions arrow, we had to create a pseudo-isodesmic situation by considering exactly one extra bond energy. Here, one T–E bond energy was chosen – thus that the final energy gain/loss represents the sum of the energy difference of the two cage topologies and the energy difference of one T–E bond being replaced by one T–T bond.

² T–E bond energies were calculated in two steps using the same quantum chemical methods for geometry optimization of all involved species and for the calculation of atomic energies: (1) atomization of H_2E for calculation of twice the E–H bond energy, (2) atomization of $T(EH)_4$ considering four times the E–H bond energy calculated before for calculation of four times the T–E bond energy.

³ For DD isomers, the ligands were considered as being involved in intramolecular O→T interactions, for AD isomers they were considered as open ligands, as observed experimentally; in case of different possible conformers regarding the relative orientation of the organic groups, the energy of the most stable one was considered throughout.

2. Details of the X-ray diffraction measurement, structure solution and refinement

General

Data were collected on diffractometer equipped with a STOE imaging plate detector system IPDS2T (**1** (second polymorph), **3**) or IPDS2 (**1**, **2**, **4**) using MoK α radiation with graphite monochromatization ($\lambda = 0.71073 \text{ \AA}$) at 100(2) K. In the case of **1**, hexagonal crystal plates were analyzed, which had to be cut in six pieces in order to separate the twinning domains. Structure solution was performed by direct methods, full-matrix-least squares refinement against F^2 using SHELXS-97 and SHELXL-97 software [S6].

Compound 1

All non-H atoms were refined using anisotropic displacement parameters. H atoms were calculated by using the standard HFIX commands 23 (CH₂ groups) or 33 (CH₃ groups). Two EADP restraints were used for the following atom pairs: C21/C31, O11/O21, in order to afford a converged fully anisotropic model. On the final difference Fourier map, the highest peak of 1.30 e/\AA^3 was located at 1.11 \AA from Te2 (the deepest hole of -2.19 e/\AA^3 was located at 0.91 \AA from Te6). The unit cell contains two crystallographically independent molecules that cannot be transferred into each other by symmetry operations due to slightly differing positions of the organic substituents.

Another dataset was obtained when pure THF was used as a reaction solvent. Apparently, a monoclinic twinned polymorph, **1a**, was thus crystallized. The twinning of the dataset was not straightforward in detection. First problems with cell choice had to be faced (the highest symmetry cell to be found was tetragonal with $a = b = 13.00$, $c = 11.63 \text{ \AA}$, $V = 1965 \text{ \AA}^3$; however, for this cell choice as well as for the lower-symmetry choices, no structure solution was found). Knowing that the compound should be similar to the already known double-decker complex [(RSn)₄S₆] (R = CMe₂CH₂COMe, cell parameters: $a = 11.666(5)$, $b = 12.701(4)$, $c = 12.359(5) \text{ \AA}$, $\beta = 90.13(3)^\circ$, $V = 1831.2(12) \text{ \AA}^3$) [S12] the corresponding monoclinic cell was chosen (cell parameters: $a = 11.633(4)$, $b = 13.033(5)$, $c = 17.361(6) \text{ \AA}$, $\beta = 131.78(5)^\circ$, $V = 1962.8(12) \text{ \AA}^3$). With this cell choice, two main twin domains could be assigned, related by the following twin law (by rows): $0.99647 \ -0.00410 \ -0.00517$, $1.01240 \ 0.01127 \ 1.01155$, $-0.98155 \ -0.98532 \ 0.01632$. This was taken into account during data integration and an HKLF5 file was generated. The data were corrected for absorption using the TWINABS routine in X-Red32 software [S11]. Interestingly, the monoclinic polymorph **1a** apparently contains also a different isomer of **1**, with all O atoms being weakly coordinated to Ge atoms.

Compound 2

All non-H-atoms were refined using anisotropic displacement parameters. H atoms were calculated by using the standard HFIX commands 23 (CH₂ groups), 33 (CH₃ groups) or 147 (acid OH groups).

The structure was found to be non-merohedrally twinned. Better refinement results were achieved when only the main twin domain was considered for data integration.

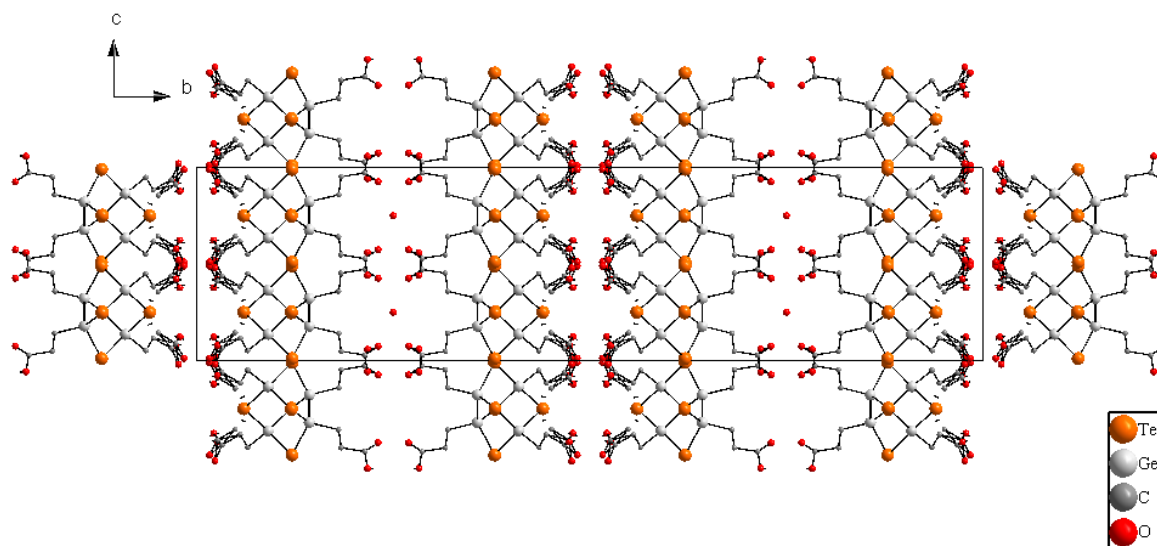
One of the two symmetry-independent CH₂COO groups was found to be disordered and split into two disorder components (refined occupancies of 0.18(2) and 0.82(2), respectively).

For the refinement, anti-bumping DFIX restraints were used ($-2.70(1)$ for O1B...O1B at $1.5-x,-y,z$ distance, $-2.00(1)$ for H2C...H2A at $x+0.5,y,1-z$ distance). A DFIX restraint was used for the carboxyl group C1A–O2A bond ($1.25(1)$ Å). However, due to considerable disorder, the relevant C–C and C–O bond lengths are not reliable. To afford a fully anisotropic model the following restraints were used: ISOR (for C3B, C1A), EADP (for the following atom pairs: C3B/C3A, O1A/O1B, O2A/O2B, C1A/C1B).

A disordered water molecule lying on special position (222 site symmetry) occupancy was refined to $0.63(5)$ value.

On the final difference Fourier map, the highest peak of $1.91 \text{ e}/\text{Å}^3$ was located at 1.00 Å from Te2 (the deepest hole of $-2.07 \text{ e}/\text{Å}^3$ was located at 0.93 Å from Te1).

Figure S1. Crystal structure of compound **2**. The view along the crystallographic a axis shows dimerisation of the carboxyl groups *via* H bonds. The O...O-distance is $2.64(2)$ Å and correlates with a “moderate” interaction specified by *Steiner* [S7] of about 16.5-60 kJ/mol.



Compound 3

All non-H-atoms were refined using anisotropic displacement parameters. H atoms were calculated by using the standard HFIX commands 13 (tertiary CH groups), 23 (CH₂ groups), 33 (CH₃ groups) or 147 (acid OH groups).

The SQUEEZE procedure [S13] was used to remove a part of heavily disordered solvent.

All C–C bond lengths were restrained to 1.54(1) Å with a DFIX restraint. Correspondingly, all carboxyl C–O bond lengths were restrained to 1.25(2) Å. Within the residual THF solvent molecule, all distances (C–C and C–O) were restrained to 1.5(1) Å.

On the final difference Fourier map, the highest peak of 0.49 e/Å³ was located at 1.69 Å from Te5 (the deepest hole of –0.47 e/Å³ was located at 1.24 Å from Te3).

Compound 4

H atoms at CH₂ and CH₃ groups were calculated by using the standard HFIX commands 23 or 33.

There are pseudo-symmetry elements in the crystal structure: pseudo-symmetry centers at 0.207, 0.373, 0.253 and 0.207, 0.123, 0.253, respectively. Also a non-crystallographic translation could be found relating the molecules with atoms Ge1 and Ge2, respectively, by a 0, 0.5, 0 translation along the [010] direction. However, no chemically reasonable structure model in any centrosymmetric space group types could be found and the structure is interpreted as a racemic twin in the non-centrosymmetric space group Cc.

The N–N bond lengths within all hydrazinium cations were restrained to 1.440(2) Å, all N–H bond lengths were restrained to 0.860(1) Å with the corresponding DFIX restraints. EADP restraints were also used to afford a fully anisotropic model (for the following atom pairs: N12/N22, N11/N21, N101/N100, C13/C43, C13/C33, N104/N105, N102/N103, N108/N109, N104/N102, N107/N106).

Amine H atoms have been found on the difference Fourier map and have been refined with $U_{eq}=1.5U_{eq}(\text{parent atom})$. Not all of the hydrazinium H atoms could be localized. This is probably due to refinement problems arising from pseudo-symmetry and the possibility of H atom disorder. Hydrazinium H atoms were gradually localized on the difference Fourier maps and carefully introduced to the model (as long as they accorded with the possible hydrogen bonding scheme). An anti-bumping DFIX restraint was used to set the H...N distance (from the –NH₂ moiety) at a value not smaller than 2.09(1) Å to ensure the right molecular geometry. The identified NH₃⁺ group H atoms were constrained with the AFIX 33 constraint. For the remaining N-bonded H atoms, no constraints were used (to avoid drift of restrained distances values). On the final difference Fourier map, the highest peak of 1.78 e/Å³ was located at 0.83 Å from Te6 (the deepest hole of –2.08 e/Å³ was located at 0.77 Å from Te8). The first 16 peaks on the difference Fourier map were located in the neighborhood of Te atoms.

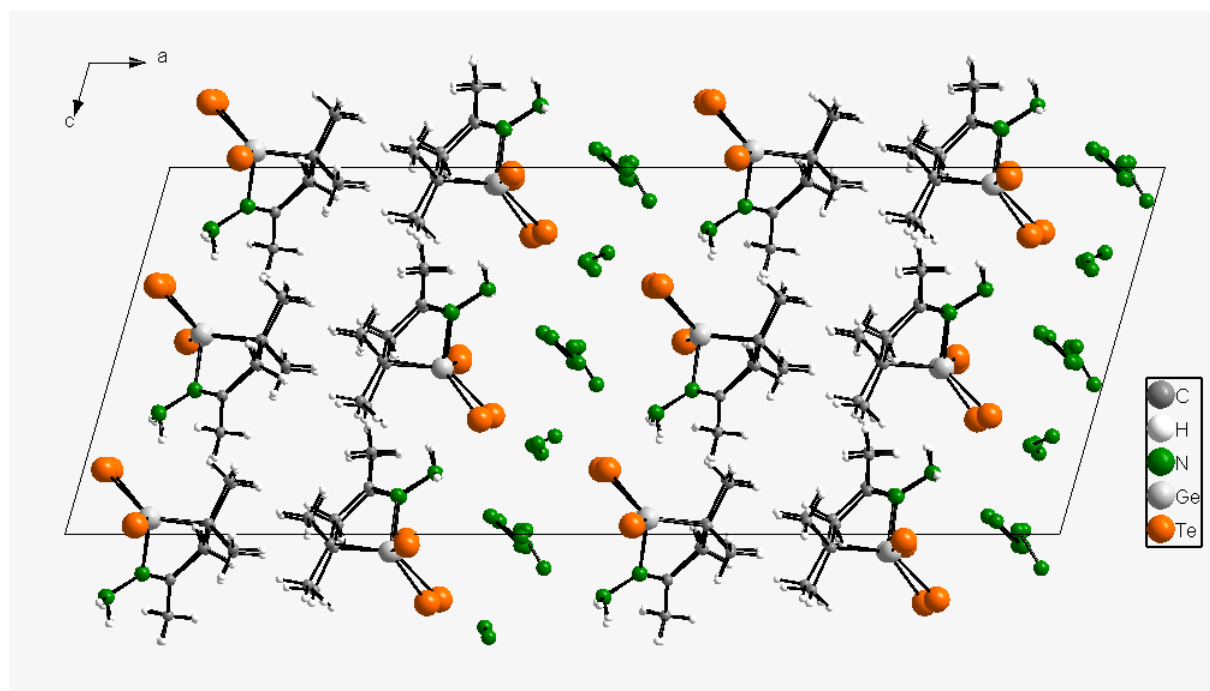


Figure S2. Crystal structure of compound 4 viewed along the *b* axis.

Table S4. Crystallographic and refinement details of **1–4** at 100K.

Compound	1	1a	2	3	4
formula	C ₂₄ H ₄₄ Ge ₄ O ₄ Te ₆	C ₂₄ H ₄₄ Ge ₄ O ₄ Te ₆	C ₁₂ H ₂₀ Ge ₄ O ₈ Te ₅ ·0.32H ₂ O	C ₂₀ H ₂₀ Ge ₄ O ₁₆ Te ₅ ·2THF	[C ₆ H ₁₃ GeN ₂ Te ₂][N ₂ H ₅]·0.5N ₂ H ₄
CCDC	794768		794769	794770	794771
M _z [g·mol ⁻¹]	1452.55	1452.55	1226.09	1588.93	490.06
crystal color/shape	orange plate (cut)	orange block	yellow block	orange needle	orange needle (cut)
crystal size [mm]	0.11x0.07x0.05	0.17x0.07x0.05	0.05x0.05x0.05	0.22x0.06x0.02	0.05x0.05x0.05
Temperature [K]	100(2)	100(2)	100(2)	100(2)	100(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	triclinic	triclinic	orthorhombic	monoclinic	monoclinic
space group	P $\bar{1}$	P $\bar{1}$	Ccca	P2 ₁ /n	Cc
a [Å]	11.052(3)	11.633(4)	10.100(3)	11.901(4)	31.866(7)
b [Å]	11.141(3)	13.033(5)	50.56(1)	23.406(6)	15.441(4)
c [Å]	15.946(4)	17.361(6)	12.418(4)	19.298(5)	12.271(4)
α [°]	89.56(3)				
β [°]	86.20(3)	131.78(5)		90.57(4)	105.94(3)
γ [°]	83.69(3)				
V [Å ³]	1947.3(9)	1963(2)	6341(3)	5375(3)	5806(3)
Z	2	2	8	4	16
ρ _{calcd} [g·cm ⁻³]	2.477	2.458	2.569	1.963	2.243
μ (MoK _α) [mm ⁻¹]	7.49	7.43	8.30	4.93	6.03
2θ range [°]	2.6–53.6	5.64–50.0	9.3–53.52	7.36–50.00	9.26–53.46
Refins measd	15301	1490	17666	32249	21516
R(int)	0.0953	0.0000 ¹	0.1274	0.2528	0.0767
indep refins	8080	6804 ¹	3302	8337	11569
obsd refins [I>2σ(I)]	4633	4517 ²	2098	2357	10471
Parameters	331	174	152	460	500
R1 [I > 2σ(I)]	0.0503	0.1115	0.0776	0.0603	0.0329
wR2 (all data)	0.1151	0.2938	0.1786	0.1418	0.0911
S (all data)	1.020	1.083	1.005	0.643	1.056
largest peak/hole [e ⁻ Å ⁻³]	1.30/-2.19	3.64/-1.70	1.90 / -2.07	0.49 / -0.47	1.78 / -2.08

¹ The dataset was twinned and of poor quality

² A HKL5 format was used for the file with reflections

3. Experimental Syntheses Details

General: All synthesis steps were performed with strong exclusion of air and external moisture (Ar atmosphere at a high-vacuum, double-manifold Schlenk line or N₂ atmosphere in a glovebox). All solvents were dried and freshly distilled prior to use.

NMR spectroscopy: NMR measurements were carried out on samples solved in deuterated solvents using a Bruker DRX 400 MHz spectrometer at 25°C. For ¹²⁵Te-NMR data, Me₂Te was used as internal standard.

UV-visible spectroscopy: UV-visible 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 samples were prepared as a solution in a quartz cuvette. The transfer from sulfide complexes to the telluride analogs **1** - **3** is reflected by smaller electronic excitation energies: in accordance with the orange color, clearly different from the colorless Sn/S or Ge/S homologues, the onset of absorption in the UV-visible spectra is observed at 2.11 (**1**) or 2.09 eV (**2**, **3**).

Raman spectroscopy: Raman spectra were recorded on a Cary Modell 83 spectrometer focused on skeleton vibrations in the range of 1500–100 cm⁻¹. The sample was prepared in a sealed capillary including argon atmosphere.

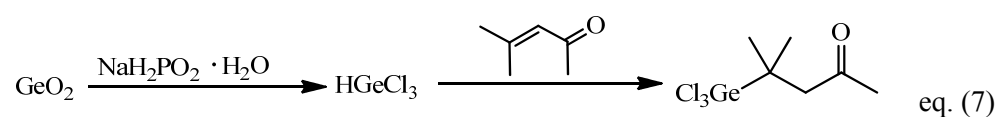
Melting point: Melting point determination was carried out in a Büchi SMP-20 with single crystals.

Energy dispersive X-ray spectroscopy (EDX analyses): EDX analyses were performed using the EDX-device Voyager 4.0 of Noran Instruments coupled with the electron microscope CamScan CS 4DV. Data acquisition was performed with an acceleration voltage of 20 kV and 100 s accumulation time. For the analyses multiple single crystals were used and the data recorded both: various times on one single crystal and various times on other single crystals.

3.1 A₂Te (A = Li, Na)

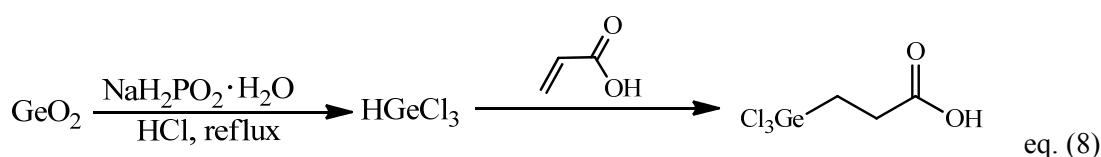
According to the standard literature method [S8], the alkaline metal was solved in liquid ammonia at –40°C and reacted over hours with the corresponding amount of tellurium. The mixture was allowed to warm up to room temperature overnight to remove the solvent.

3.2 Cl₃GeCMe₂CH₂COMe



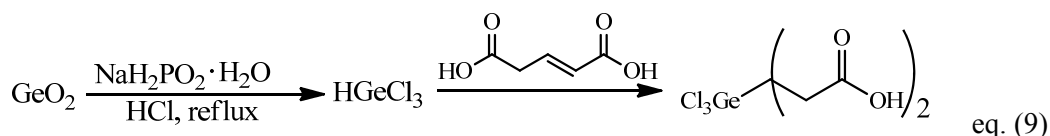
The synthesis was performed according to literature [S9]: 1 g (9.53 mmol) of GeO₂ was added to 30 mL hydrochloric acid, and refluxed to give a lightly yellow solution. Subsequently, 10.10 mmol, i.e. 2 equiv. of NaH₂PO₂·H₂O were added. The mixture was then cooled to 0°C, and 1.2 equiv. of mesityl oxide were added. The reaction mixture was stirred overnight at room temperature. During this time, the product precipitated. The white product was filtered off and dried under high vacuum. After extraction with diethyl ether and removal of the solvent, the pure product was obtained. Yield: 69%, 1.83g (6.57 mmol) NMR (CDCl₃, 300MHz): ¹H: 1.39 (s, 6H, CMe₂), 2.25 (s, 3H, CH₃), 2.87 ppm (s, 2H, CH₂); ¹³C: 24.21 (CMe₂), 29.68 (Me), 43.37 (GeC), 53.70 (CH₂), 206.7 ppm (CO).

3.3 Cl₃GeCH₂CH₂COOH



The synthesis was performed according to literature [S9]. 1 g (9.53 mmol) of GeO₂ was added to 30 mL hydrochloric acid, and refluxed to give a lightly yellow solution. Subsequently, 10.10 mmol, i.e. 2 equiv. of NaH₂PO₂·H₂O were added. The mixture was then cooled to 0°C, and 1.2 equiv. of acrylic acid were added. The reaction mixture was stirred overnight at room temperature. During this time, the product precipitated. The white solid was filtered off and dried under high vacuum. After extraction with diethyl ether and removal of the solvent, the pure product was obtained. Yield: 69%, 1.83g (6.57 mmol) NMR (CDCl₃, 300MHz): ¹H: 1.39 2.30 (t, 2H, CH₂), 2.86 ppm (t, 2H, CH₂); ¹³C: 27.33 (CH₂), 27.86(CH₂), 176.6 ppm (COOH).

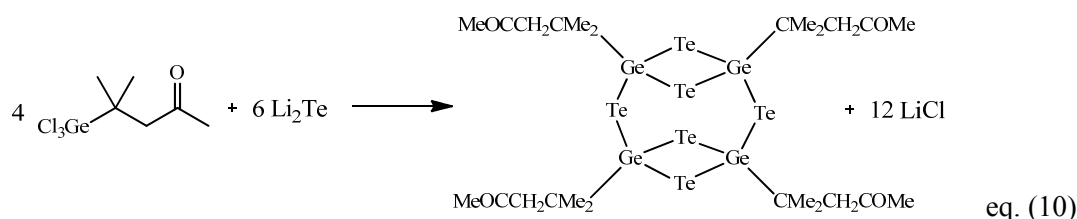
3.4 Cl₃GeCH(CH₂COOH)₂



The synthesis was performed similar to literature [S10]. 0.57 g (5.047 mmol) of GeO₂ were added to NaH₂PO₂·H₂O (10.10 mmol, 2 equiv.) in 50 cm³ of an HCl solution (37% in water), and 15 cm³ of water in a round bottom flask. The reaction mixture was refluxed to give a transparent solution. It was then cooled to 0°C, and 1.2 equiv. of glutaric acid were added, along with 30 cm³ of diethyl ether. The reaction mixture was stirred overnight at room temperature. During this time the product precipitated. The white solid was filtered off and dried under high vacuum. After extraction with diethyl ether and removal of the solvent, the pure product was obtained.

Yield: 86%, 1.35 g (4.34 mmol) NMR (CDCl₃, 300MHz): ¹H: 1.45 (m, 1H, HGeCl₃), 2.83 (m, 4H, HC-(CH₂COOH)₂) ppm; ¹³C: 172.5 (C=O), 33.6 (CH₂), 33.0 (CH) ppm.

3.5 Compound 1: [(CMe₂CH₂COMe)Ge]₄Te₆



A solution of Cl₃GeCMe₂CH₂COMe (0.25 g, 0.89 mmol) in THF (20 mL) was added slowly to a suspension of Li₂Te (0.188 g, 1.335 mmol) in acetone (20 mL) at 20°C. After 15 h of stirring, the reaction mixture was filtered. Orange crystals of **1** were obtained within 3 days, upon layering of the clear orange solution by *n*-octane. Yield: 0.124 g (0.08 mmol, 38%).

Melting point: 178 °C

MS: ESI *m/z* = 1161.1 (M⁺)

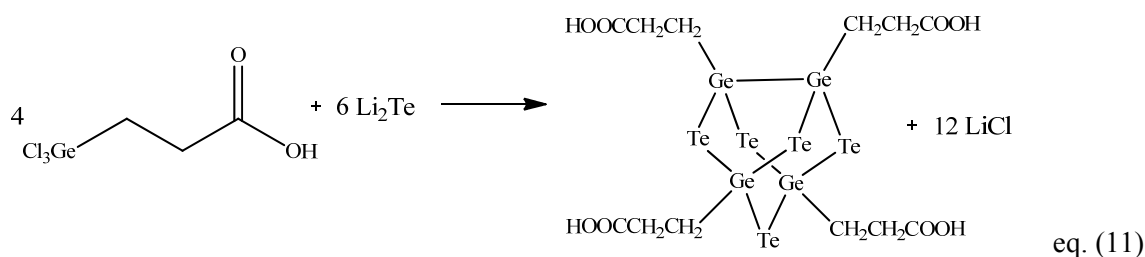
EDX: Ge : Te calc.: 1 : 1.50 exp.: 1 : 1.51

CHN: calc.: C 19.84 % H 3.06 % N 0.00 %

exp.: 20.75 % 3.46 % 0.23 %

UV-vis: E_{onset} = 2.11 eV, E_{plateau} = 2.75 eV

3.6 Compound 2: [(CH₂CH₂COOH)Ge]₄Te₅·0.32H₂O



A suspension of Li₂Te (0.211 g, 1.485 mmol) in THF (15 mL) was cooled to 5°C and reacted with Cl₃GeCH₂CH₂COOH (0.25 g, 0.99 mmol) in THF (10 mL). By-products were filtered off after 15 h of stirring, and the clear orange solution was concentrated to 3.5 mL. Orange crystals of **2** were obtained upon layering by *n*-hexane within 5 days. Yield: 0.096 g (0.08 mmol, 32%).

Melting point: 172 °C

MS: ESI *m/z* = 1221.1 (M)

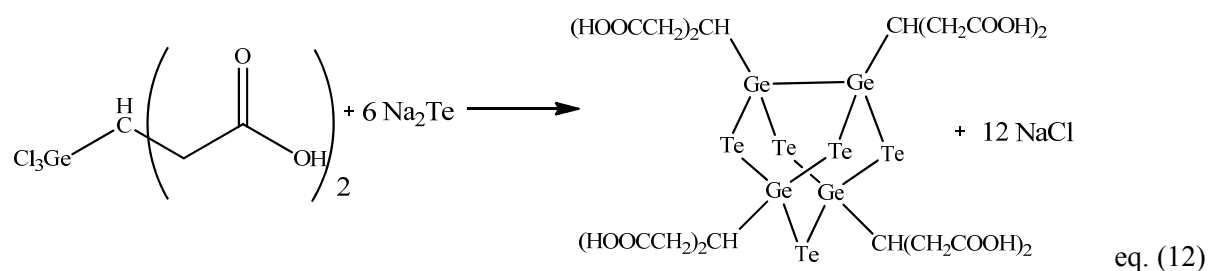
EDX: Ge : Te calc.: 1 : 1.25 exp.: 1 : 1.33

CHN: calc.: C 11.80 % H 1.65 % N 0.00 %

exp.: 12.45 % 1.81 % 0.30 %

UV-vis: E_{onset} = 2.09 eV, E_{plateau} = 2.77 eV

3.7 **Compound 3:** $[(CH(CH_2COOH)_2)Ge]_4Te_5 \cdot 2THF$



A suspension of Na_2Te (0.084 g, 0.48 mmol) in THF (10 mL) was cooled to 5°C and reacted with $Cl_3GeCH(CH_2COOH)_2$ (0.08 g, 0.32 mmol) in THF (10 mL). By-products were filtered off after 15 h of stirring, and the clear orange solution was concentrated to 3.5 mL. Orange crystals of **2** were obtained upon layering by *n*-hexane within 5 days. Yield: 0.098 g (0.07 mmol, 21%).

Melting point: 172 °C

MS: ESI $m/z = 1450.3$ (M)

EDX: Ge : Te calc.: 1 : 1.25 exp.: 1 : 1.33

CHN: calc.: C 11.80 % H 1.65 % N 0.00 %

exp.: 12.45 % 1.81 % 0.30 %

UV-vis: $E_{onset} = 2.09$ eV, $E_{plateau} = 2.77$ eV

NMR (THF- d^8 , 300MHz): 1H : 2.63-2.80(m, 2H, CH_2), 2.80-2.90 ppm (m, 2H, CH_2), 2.90-3.04 (m, 2H, CH); 11.02 (bs, 2H, COOH); ^{13}C : 28.24 (CH), 29.16 (CH), 36.77(CH_2), 39.16(CH_2), 172.55 (COOH), 174.38 ppm (COOH); ^{125}Te -NMR 22.08 Te-(GeR-Te2) -98.05 Te-(Ge-Ge).

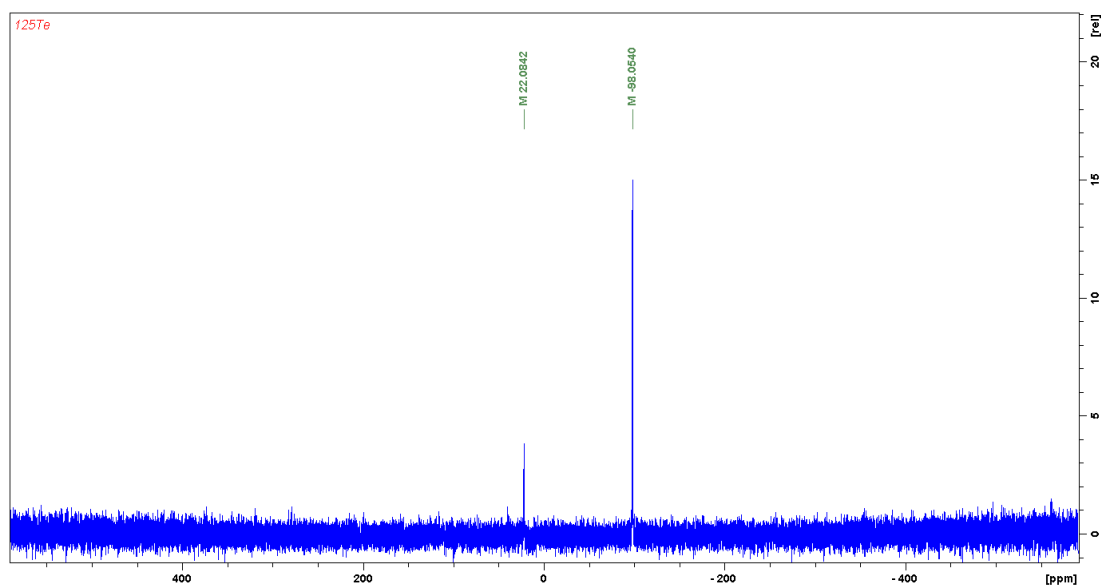
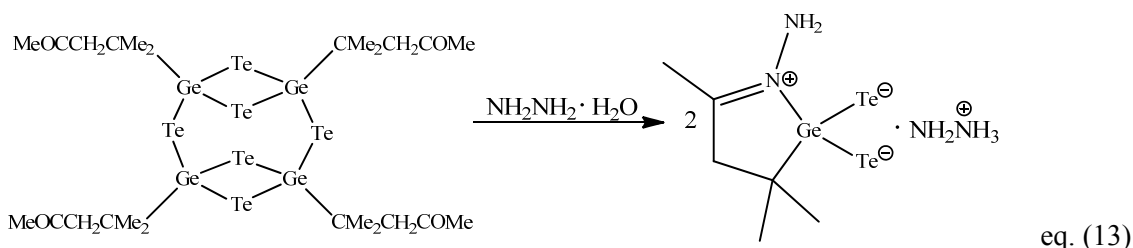


Figure S3. ^{125}Te -NMR spectrum of compound **3**.

3.8 Compound 4: $[(C_6H_{13}N_2)GeTe_2][NH_2NH_3]^+ \cdot 0.5N_2H_4$



Crystals of **1** (0.05 g, 0.039 mmol) were dissolved in hydrazine hydrate (3 mL) within an ultrasonic bath. After 4 h of stirring, the obtained, orange solution was concentrated to half volume. Dark orange crystals of **4** were obtained by storing the solution at $-4^{\circ}C$ within 2 days. Yield: 2.99 mg ($6 \cdot 10^{-6}$ mol, 8%).

EDX: Ge : Te calc.: 1 : 1.20 exp.: 1 : 1.19

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