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

Samuel Heimann, Małgorzata Hołyńska and Stefanie Dehnen*

Received 8th September 2010, Accepted 17th November 2010 DOI: 10.1039/c0cc03727c

Unprecedented noradamantane-type compounds $[(R^{2,3}Ge)_4Te_5]$ $(R^2 = CH_2CH_2COOH, R^3 = CH(CH_2COOH)_2)$, containing a Ge-Ge bond, yield from reactions of $R^{2,3}GeCl_3$ with Na₂Te or Li₂Te in THF, while reactions with R¹GeCl₃ $(R^1 = CMe_2CH_2COMe)$ afford a double-decker-type cage $[(R^3Ge)_4Te_6]$; by reaction with hydrazine, the latter reacts to the hydrazone functionalized, monomeric anion $[(R^4Ge)Te_2]^ (R^4 = CMe_2CH_2CNNH_2Me)$.

Germanium and tin sesquichalcogenide cages with organic decoration, $[(RT)_4E_6]$ (T = Ge, Sn; E = S), were first synthesized in 1903, and structurally characterized in 1968.¹ Since then, they have attracted attention due to intriguing structural, chemical and physical properties.² In the meantime, several examples were reported, containing widely non-reactive organic groups R = alkyl, aryl, CF₃, C₆F₅, C(SiMe₃)₃.^{3–5} It was further shown that thiotetrelate cages can be useful precursors for the synthesis of ternary M/T/E complexes like [(PhT)₂(CuPMe₂Ph)₆S₆].⁶ Very recently, the research field was extended (a) toward thiogermanate and thiostannate complexes with reactive organic groups,^{7,8} in order to generate hybrid complexes and networks by reactions with reagents of complementary functionalization,^{7,9} and (b) toward functionalized ternary Cu/T/S (T = Ge, Sn)⁷ or M/Ge/S aggregates (M = Ni, Pd).^{10–12}

Still, most investigations on the tetrel sesquichalcogenides have so far been limited to the sulfide compounds, while the corresponding selenium and tellurium compounds have not been examined to a significant amount. The only examples so far are $[(RSnE)_2CR'_2]_2$ (R = Ph, CH₂SiMe₃, Me; R' = H, Me; E = S, Se, and/or Te),¹³ $[(R''T)_4Se_6]$ (T = Si, Ge; R'' = Thex = 1,1,2-Me₃C₃H₅, *i*C₅H₁₁, CF₃)⁵ and $[(R'''Ge)_4Te_6]$ (R''' = 2,4,6*i*Pr₃C₆H₂).¹⁴ These heavier homologues are expected to exhibit different physical and chemical properties in comparison to the sulfides; in particular, with tuneable solubility and reactivity owing to the organic ligands, they might be attached to biochemical molecules, such as proteins, to become useful tools for the *ab initio* phasing of their crystal structures.¹⁵

Herein, we report syntheses, characterization and reactivity of the first Ge/Te complexes with functional organic ligands.

Hans-Meerwein-Strasse, D-35043 Marburg, Germany.

The results indicate that it is not possible to simply transfer the characteristics of the Ge/S or Sn/S systems to Ge/Te.

While Ge/S or Sn/S complexes were generated in water or water/acetone mixtures,^{7,8} the preparation of the related Ge/Te compounds from RGeCl₃ precursors had to be carried out in THF due to the tendency of A₂Te (A = Li, Na) to decompose under formation of elemental tellurium in ROH (R = H, Me, Et). As shown in Scheme 1, $[(R^1Ge)_4Te_6]$ (1: R¹ = CMe₂CH₂COMe) and $[(R^{2,3}Ge)_4Te_5]$ (2: R² = CH₂CH₂COOH, 3: R³ = CH(CH₂COOH)₂) were produced by reactions of commercially available α , β -unsaturated carboxylic acids with HGeCl₃, and ensuing *in situ* reactions with Na₂Te or Li₂Te, respectively. $[N_2H_5][(R^4Ge)Te_2]\cdot 0.5N_2H_4$ (4: R⁴ = CMe₂CH₂CNNH₂Me) was obtained by a reaction of 1 with a solution of hydrazine in THF ($c = 1 \text{ mol } 1^{-1}$).

Compounds 1–4 were characterized by standard analytical methods and by single-crystal X-ray diffraction (see ESI†). The molecular structure of $[(R^1Ge)_4Te_6](1; R^1 = CMe_2CH_2COMe)$ is illustrated in Fig. 1.

Compound 1 adopts a double-decker-type structural motif (DD), with two coplanar Ge₂Te₂ four-membered rings (sum of angles: 359.9°) that are bridged by two additional Te ligands, similar to recently reported $[(R^{1}Sn)_4S_6]^{7,8}$ or the above mentioned $[(R''Ge)_4Te_6]^{.14}$ Bond lengths and angles are in good agreement with those found in other Ge/Te compounds.¹⁶ As in $[(R^1Sn)_4S_6]$, some of the C=O groups at the organic substituent in 1 are involved in an intramolecular Ge···O coordination, thereby increasing the coordination number of the Ge atom to five, which is much rarer in Ge compounds than in homologue Sn complexes. Thus, 1 differs from organo functionalized Ge sesquisulfides, all of which possess a Ge/S adamantane-type skeleton (AD) under ambient conditions.^{5,7,8}

According to quantum chemical investigations using DFT methods¹⁷ (program system Turbomole,¹⁸ Table 1), the DD-type structure is energetically favored over the AD-type for all $[(R^1Sn)_4E_6]$ complexes, on account of relatively small Sn···O distances (exp. for E = S: 2.614(5)-2.672(4) Å), representing non-negligible bonding interactions.⁷ For $[(R^{1.2}Ge)_4E_6]$ in contrast, the AD-type is preferred, owing to only weak

$$\operatorname{GeO}_2 \xrightarrow{a} \operatorname{HGeCl}_3 \xrightarrow{b} \operatorname{RGeCl}_3 \xrightarrow{c} [(\operatorname{RGe})_4\operatorname{Te}_6] (1) \\ [(\operatorname{RGe})_4\operatorname{Te}_5] (2, 3)$$

Philipps-Universität Marburg, Fachbereich Chemie and

Wissenschaftliches Zentrum für Materialwissenschaften (WZMW),

E-mail: dehnen@chemie.uni-marburg.de; *Fax:* +49 6421 2825653; *Tel:* +49 6421 2825751

[†] Electronic supplementary information (ESI) available: Details on quantum chemical investigations, X-ray diffraction, spectroscopy/ spectrometry, syntheses of 1–4. See DOI: 10.1039/c0cc03727c



Fig. 1 Molecular structure of one of the two symmetry independent molecules of 1. Selected distances [Å] and angles $[\degree]$: Ge–Te 2.556(2)–2.6295(18), Ge–C 1.975(13)–1.999(13), Ge–··O 2.82(1)–2.88(1).

Ge···O interactions (exp. for 1: 2.82(1)–2.88(1) Å). Indeed, $[(R^{1,2}Ge)_4S_6]$ were reported to crystallize in the AD-type.⁷ For R^1 and E = Te, both structures are nearly isoenergetic and might be observed—with the DD-type being realized here.

Different to the result obtained at the synthesis of 1, another cage type was observed upon reactions of acid functionalized trichlorogermyl compounds $R^{2,3}GeCl_3$ ($R^2 = CH_2CH_2COOH$, $R^3 = CH(CH_2COOH)_2$) with Na₂Te or Li₂Te: the molecular structures of [($R^{2,3}Ge)_4Te_5$] (2: R^2 , 3: R^3) are based on a noradamantane-type cage (NA), comprising a Ge–Ge bond instead of a Ge–Te–Ge bridge. Besides the characteristic Ge–Te vibrations at 80, 110, and 140 cm⁻¹,¹⁶ which are present in the Raman spectra of 1–3, a weak additional band was observed in the spectrum of 3 at 263 cm⁻¹, which can be assigned to the Ge–Ge vibration (260–270 cm⁻¹).^{2,19} Fig. 2 shows the molecular structure of the two complexes. Until now, this topology has been restricted to silicon selenides that have, however, been synthesized from precursors containing a Si–Si bond (Scheme 2).²⁰

The observed type of an in situ Ge-Ge bond formation under ambient conditions is-to the best of our knowledgeunique. So far, organosubstituted Ge-Ge bonds were formed via dehalogenation reactions of organyl-halogermanes-with Na or Na/K alloy,²¹ diisopropyltelluride,²² or electrochemically²³-or by catalytic dehydrogenation of organylhydrogermanes.²⁴ For Ge-Ge bonds in chalcogenide compounds, the examples are even rarer. Inorganic Ge-Ge bond formation is known to result from high temperature reactions, such as for the formation of Na₈Ge₄Te₁₀.²⁵ With organic ligands, this is not possible; corresponding reactions were therefore performed by direct coupling of RGeCl₃ using soft reduction reagents like $Mg/MgBr_2$ (R = 1-ethyl-1-methylpropyl, for instance).²⁶ For the formation of 2 and 3, the negative redox potential of Te^{2-} $(-1.143 \text{ V})^{27}$ might have enabled the formation of $[R^{2,3}GeCl_2]^-$ with subsequent Wurtz-type coupling.

DFT calculations helped to answer the following questions: (1) Are the NA-type cages indeed energetically favored over the corresponding AD-type or DD-type complexes? (2) Is the cage type dependent on the ligand type? The questions were answered by calculating the reaction energies of the following hypothetical—reactions (Table 1; E^{at} represents an E atom; the non-isodesmic situation is accounted for by considering the respective Ge–E bond energy, as calculated using the same methods; note that the reactions do not represent the formation mechanism which would require the consideration of elemental E_x oligomers or polymers; for further details see ESI†):

$$[(\mathbf{RT})_4 \mathbf{E}_6]^{\mathrm{AD}} \to [(\mathbf{RT})_4 \mathbf{E}_6]^{\mathrm{DD}}, \Delta E_{\mathrm{DD-AD}}$$
(1)

$$\left[(\mathbf{RT})_4 \mathbf{E}_6 \right]^{\text{DD}} \rightarrow \left[(\mathbf{RT})_4 \mathbf{E}_5 \right] + \mathbf{E}^{\text{at}}, \Delta E_{\text{NA-DD}}$$
(2)

$$\left[(\mathbf{RT})_4 \mathbf{E}_6\right]^{\mathrm{AD}} \rightarrow \left[(\mathbf{RT})_4 \mathbf{E}_5\right] + \mathbf{E}^{\mathrm{at}}, \Delta \mathbf{E}_{\mathrm{NA-AD}} \tag{3}$$

The energy values given in Table 1 indicate that the experimental observation of the formation of an NA-type complex instead of the DD-type or AD-type alternatives is indeed only expected for exactly this particular $RT/E = R^{1}Ge/Te$ combination (highlighted by bold numbers in Table 1), i.e. for telluridogermanate complexes ligated by carboxyl terminated organic ligands, such as 2. This has to be put down to both the T/E combination and the ligand type. The first allows for a preference of one T-E and the new T-T bond over two T-E bonds. Second, the intramolecular $O \rightarrow T$ interaction, which is only observed for DD-type complexes, leads to a preference of this cage type only for stannates with R¹ ligands, terminated by -COMe; for germanates and/or ligands with -COOH groups, the stabilizing effect is much smaller to result in a general preference for AD-type cages. Thus the $O \rightarrow T$ interaction cannot overcompensate the energetic preference of the NA formation in the R²Ge/Te case. The study also shows that an energetic preference of DD-type complexes is only given for $Sn/E/R^1$. However, the higher stability of AD-type cages decreases from E = S through Se to Te in all cases, leading to a very small energetic preference of only 1.71 kJ mol⁻¹ at $T/E/R = Ge/Te/R^{1}$. Therefore, crystallization of 1 as DD-type might result from additional effects attributable to the crystal formation.

It was previously shown that DD-type T/E complexes that are ligated by carbonyl functionalized organic groups react readily with hydrazines under formation of hydrazone derivatives.⁷ However, reactions of **1** with hydrazine showed once more the inequality of the Ge/Te system when compared to the Sn/S congener: instead of the perpetuation of the Ge/Te-skeleton in **1**,

Table 1 Energies of the isomerization of AD to DD-type isomers [eqn (1)], and reaction energies for the reaction of DD to NA-type clusters [eqn (2)], or of AD to NA-type clusters [eqn (3)], as resulting from DFT calculations for all combinations of tetrels T = Ge, Sn and chalcogens E = S, Se, Te with organic ligands $R = R^1$ or R^2 . Values are given in kJ mol⁻¹.

T/E	$\mathbf{R}^1 = \mathbf{CMe}_2\mathbf{CH}_2\mathbf{COMe}$			$R^2 = CH_2CH_2COOH$		
	$\Delta E_{ m DD-AD}$	$\Delta E_{ m NA-DD}$	$\Delta E_{ m NA-AD}$	$\Delta E_{ m DD-AD}$	$\Delta E_{ m NA-DD}$	$\Delta E_{ m NA-AD}$
Ge/S	19.42	70.01	89.43	23.27	40.81	64.08
Ge/Se	11.35	47.41	58.76	16.82	13.27	30.09
Ge/Te	1.71	19.52	21.23	10.41	-19.46	-9.06
Sn/S	-23.71	104.76	81.06	9.60	68.86	78.46
Sn/Se	-27.77	85.91	58.14	4.29	49.80	54.08
Sn/Te	-29.04	55.96	26.92	2.11	20.00	22.11



Fig. 2 Molecular structures of 2 (left hand side) and 3 (right hand side); disorder and H atoms omitted for clarity. Selected distances [Å]: 2: Ge–Te 2.555(2)–2.575(2), Ge–Ge 2.451(2), Ge–C 1.979(12)–1.991(11); 3: Ge–Te 2.560(3)–2.593(3), Ge–Ge 2.482(4), Ge–C 1.972(18)–2.01(2).



Scheme 2 Synthesis of Si/Se noradamantane-type complexes.²⁰



Fig. 3 Molecular structure of the anion in **4**. The $[N_2H_5]^+$ cation is not shown. Selected distances [Å]: Ge–Te 2.468(2)–2.513(2), Ge–C 1.998(13)–2.021(13), Ge–N 2.027(12)–2.038(12).

another reaction took place here, that ended up with the formation of the hydrazonium salt **4** of the functionalized monomeric anion $[R^4GeTe_2]^-$ (Fig. 3); in the latter, the organic substituent also establishes a five-membered ring including a Ge–N bond (2.027(12)-2.038(12) Å).

The observed results illustrate that—in contrast to the known (RGe)/S system—an $O \rightarrow Ge$ or $N \rightarrow Ge$ interaction is possible in (RGe)/Te complexes, owing to longer Ge–E bonds and thus lower steric repulsion; as a consequence, unexpected products adopting a DD-type Ge/E skeleton or representing a monomeric unit are observed that feature these intramolecular donor–acceptor bonds. Moreover, for COOH-terminated ligands, uncommon NA-type Ge/Te complexes bearing a Ge–Ge bond are preferred for this particular (RT)/E combination, as confirmed by DFT calculations.

We thank the German Science Foundation (DFG) for financial support and Dr K. Harms for valuable help with the twinned X-ray structure analyses.

Notes and references

 (a) P. Pfeiffer and R. Lehnardt, *Chem. Ber.*, 1903, 36, 3027;
 (b) C. Dorfelt, A. Janeck, D. Kobelt, E. F. Paulus and H. Scherer, *J. Organomet. Chem.*, 1968, 14, P22.

- 2 D. A. Armitage, in *The chemistry of organic silicon compounds*, ed. S. Patai and Z. Rappoport, John Wiley & Sons Ltd., London, 1989, pp. 1401–1409.
- 3 (a) D. Kobelt, E. F. Paulus and H. Scherer, Acta Crystallogr., Sect. B, 1972, 28, 2323; (b) A. G. Davies, L. Smith and P. J. Smith, J. Organomet. Chem., 1972, 39, 279; (c) H. Berwe and A. Haas, Chem. Ber., 1987, 120, 1175; (d) W. Ando, T. Kadowaki, Y. Kabe and M. Ishii, Angew. Chem., Int. Ed. Engl., 1992, 31, 59; (e) M. Weidenbruch, J. Schlaefke, A. Schäfer, K. Peters, H. G. von Schnering and H. Marsmann, Angew. Chem., Int. Ed. Engl., 1994, 33, 1846; (f) W. Ando, T. Kadowaki, A. Watanabe, M. Choi, Y. Kabe, T. Erata and M. Ishii, Nippon Kagaku Kaishi, 1994, 3, 214; (g) K. Wraage, T. Pape, R. Herbst-Irmer, M. Noltemeyer, H.-G. Schmidt and H. W. Roesky, Eur. J. Inorg. Chem., 1999, 869; (h) C. Wagner, C. Raschke and K. Merzweiler, Appl. Organomet. Chem., 2004, 18, 147.
- 4 (a) K. Moedritzer, Inorg. Chem., 1967, 6, 1248; (b) R. H. Benno and C. J. Fritchie, Jr., J. Chem. Soc., Dalton Trans., 1973, 543; (c) A. Haas, H.-J. Kutsch and C. Krüger, Chem. Ber., 1987, 120, 1045; (d) B. Krebs, Angew. Chem., Int. Ed. Engl., 1983, 22, 113; (e) M. N. Bochkarev, L. P. Maiorova, N. S. Vyazankin and G. A. Razuvaev, J. Organomet. Chem., 1974, 82, 65; (f) S. Pohl, Angew. Chem., Int. Ed. Engl., 1976, 15, 162; (g) S. Pohl, U. Seyer and B. Krebs, Z. Naturforsch., B, 1981, 36, 1432.
- 5 (a) M. Unno, Y. Kawai, H. Shioyama and H. Matsumoto, Organometallics, 1997, 16, 4428; (b) B. Célariès, G. Rima, L. Court, C. Lion and J.-D. Laval, Met.-Based Drugs, 2001, 8, 199.
- 6 R. Hauser and K. Merzweiler, Z. Anorg. Allg. Chem., 2002, 628, 905.
- 7 Z. Hassanzadeh Fard, L. Xiong, C. Müller, M. Hołynska and S. Dehnen, *Chem.-Eur. J.*, 2009, **15**, 6595.
- 8 Z. Hassanzadeh Fard, C. Müller, T. Harmening, R. Pöttgen and S. Dehnen, Angew. Chem., Int. Ed., 2009, 48, 4441.
- 9 Z. Hassanzadeh Fard, M. R. Halvagar and S. Dehnen, J. Am. Chem. Soc., 2010, 32, 2848.
- 10 (a) T. Matsumoto, Y. Nakaya and K. Tatsumi, *Organometallics*, 2006, **25**, 4835; (b) T. Matsumoto, Y. Matsui, M. Ito and K. Tatsumi, *Inorg. Chem.*, 2008, **47**, 1901; (c) T. Matsumoto, Y. Matsui, M. Ito and K. Tatsumi, *Chem.–Asian J.*, 2008, **3**, 607.
- 11 M. R. Halvagar, Z. Hassanzadeh Fard, L. Xiong and S. Dehnen, *Inorg. Chem.*, 2009, 48, 7373.
- 12 C. Pöhlker, I. Schellenberg, R. Pöttgen and S. Dehnen, Chem. Commun., 2010, 46, 2605.
- 13 D. Dakternieks, K. Jurkschat, H. Wu and E. R. T. Tiekink, Organometallics, 1993, 12, 2788.
- 14 G. Ramaker, W. Saak, D. Haase and M. Weidenbruch, Organometallics, 2003, 22, 5212.
- 15 (a) R. Caliandro, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, A. Mazzone and D. Siliqi, J. Appl. Crystallogr., 2008, 41, 548; (b) A. Perrakis, R. Morris and V. S. Lamzin, Nat. Struct. Biol., 1999, 6, 5.
- 16 M. Kuchta and G. Parkin, J. Chem. Soc., Chem. Commun., 1994, 1351.
- 17 W. Koch and M. C. Holthausen, A Chemist's Guide to Density Functional Theory, Wiley-VCH, 2001.
- 18 TURBOMOLE V5.10, Turbomole GmbH, Karlsruhe, 2008.
- 19 J. Weidlein, U. Müller and K. Dehnicke, *Schwingungsspektroskopie*, Georg Thieme Verlag, Stuttgart, 2nd edn, 1988, p. 46.
- 20 U. Herzog and G. Rheinwald, J. Organomet. Chem., 2001, 628, 133.
- 21 C. Eabom and K. C. Pandle, J. Chem. Soc., 1960, 3200.
- 22 I. S. Tulokhonova and M. G. Voronkov, *Inorg. Chem. Commun.*, 1998, **10**, 379.
- 23 M. Tanaka, T. Hoomashi, T. Hayashi and T. Sakakura, *Appl. Organomet. Chem.*, 1988, 4, 291.
- 24 (a) V. V. Jouikov, Usp. Khim., 1997, 66, 564; (b) M. Tanabe, N. Ishikawa, M. Hanzawa and K. Osakada, Organometallics, 2008, 27, 5152.
- 25 B. Eisenmann, H. Schäfer and H. Schwerer, Z. Naturforsch., B, 1983, 38, 924.
- 26 A. Sekiguchi, T. Yatabe, H. Kamatani, C. Kabuto and H. Sakurai, J. Am. Chem. Soc., 1992, 15, 6260.
- 27 S. G. Bratsch, J. Phys. Chem. Ref. Data, 1989, 18, 1.