Synthesis and structure of a novel pentacoordinate organogermanium compound

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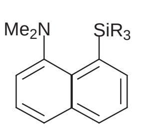
Reaction between Bu^tGeCl_3 and mercaptoacetic acid afforded a novel type of pentacoordinate germanium compound *via* $Bu^tGe(SCH_2CO_2H)_3$ which loses one mole of SCH_2CO_2H to afford the pentacoordinate species.

Hypercoordination of organosilicon compounds has been extensively investigated by Corriu and coworkers.[1] Thus, they described a variety of penta-, hexa- or hepta-coordinate silicon compounds where in most cases the donor is a nitrogen moiety (*e.g.* dimethylamino), and the geometrical relation between the silicon and the donor is more or less sterically congested as is the case with 1,8-disubstituted naphthalenes **1**[2] or *o*-substituted tribenzylsilanes **2**.[3,4] They have shown that hypercoordination was also observed for *o*-substituted tribenzylgermanes **3**. We recently reported that, in the related compounds **4** and **5**, the germanium atom is either hexa- or hepta-coordinate although the incipient bonding between germanium and oxygen or sulfur is not very strong.[5]



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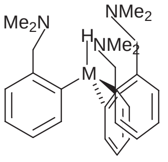
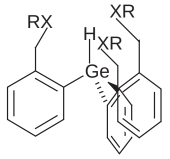
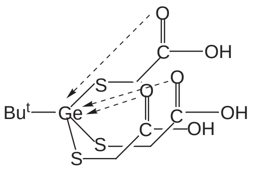


2 M = Si
3 M = Ge

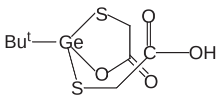


4 X = O
5 X = S

These findings prompted us to examine a further possibility; *i.e.* to observe hypercoordination of germanium atom where the geometrical relation between germanium and the donor atoms is more flexible. Initially we expected that the reaction of *tert*-butyltrichlorgermane (Bu^tGeCl_3) with mercaptoactetic acid ($HSCH_2CO_2H$) (molar ratio 1 : 3) under basic conditions would afford 2,2′,2″-[*tert*-butylgermanetriyltris(thio)]trisacetic acid, $Bu^tGe(SCH_2CO_2H)_3$ which would form heptacoordinate germanium species **6**.



6



7

The product, (colorless crystals, mp 152–154 °C from ethyl acetate) corresponds, however, to the molecular formula $C_8H_{14}GeO_4S_2$ [mass spectrum (FBMS): m/z = 310.9630 $(M + H)^+$; calc. for $C_8H_{14}{}^{72}GeO_4S_2$ = 310.9633], indicating the loss of one mole of $HSCH_2CO_2H$. The product was confirmed by X-ray analysis† as 2-(2-*tert*-butyl-5-oxo-1,3,2-oxathiagermolan-2-ylthio)acetic acid **7**. It is likely that **6** was indeed formed since its yield was substantially decreased when lower amounts (*e.g.* 1 : 2) of mercaptoacetic acid were used. Subsequently an intramolecular nucleophilic substitution takes place on germanium, where one of the $-SCH_2CO_2H$ moieties of **6** acts as a nucleophile while the other is the leaving group to give **7**.

The ORTEP drawing of **7** is shown in Fig. 1, while the molecular packing in crystal is depicted in Fig. 2. The question

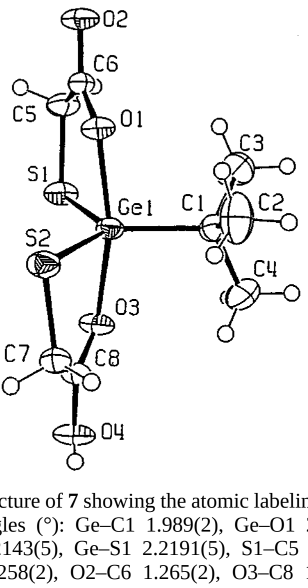


Fig. 1 Molecular structure of **7** showing the atomic labeling. Relevant bond lengths (Å) and angles (°): Ge–C1 1.989(2), Ge–O1 2.045(1), Ge–O3 2.043(1), Ge–S2 2.2143(5), Ge–S1 2.2191(5), S1–C5 1.808(2), S2–C7 1.810(2), O1–C6 1.258(2), O2–C6 1.265(2), O3–C8 1.259(2), O4–C8 1.262(2); C1–Ge–O3 98.89(6), C1–Ge–O1 94.39(6), O3–Ge–O1 166.71(5), C1–Ge–S2 119.73(5), O3–Ge1–S2 86.73(4), O1–Ge1–S2 86.91(4), C1–Ge1–S1 120.05(5), O3–Ge1–S1 86.25(4), O1–Ge1–S1 86.88(4), S2–Ge1–S1 120.19(2), C5–S1–Ge1 97.97(6), C7–S2–Ge1 96.46(6).

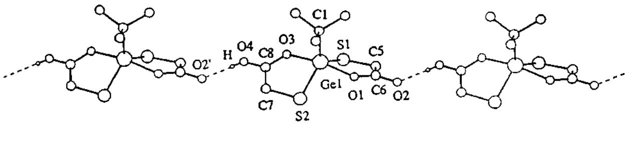


Fig. 2 Molecular packing of **7**. Intermolecular hydrogen bonds are shown by dotted lines. Important distances (Å) and angle (°): O4–H 0.74, H–O2′ 1.73, O4–O2′ 2.453(2); O4–H–O2′ 165.9.

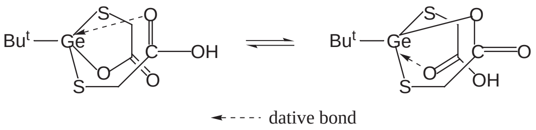
of whether the carbonyl oxygen or the hydroxyl oxygen is coordinated to Ge was resolved by the location of the hydrogen atom which was achieved by refining the analysis.‡ The result shown in Fig. 2 is very conclusive; there is a hydrogen atom between O4 of one molecule and O2 of the adjacent molecule (O2′) to indicate hydrogen bonding in **7** between the CO_2H of one molecule and the lactone carbonyl oxygen of an adjacent molecule. Thus it is the carbonyl oxygen which was coordinated to Ge.

Characteristic points observed for **7** are as follows: (1) The germanium atom is pentacoordinate with trigonal bipyramidal structure. (2) The Ge1–S1, Ge1–S2 and Ge1–C1 bonds are equatorial while the Ge1–O1 and Ge1–O3 bonds are apical with equal length (*ca*. 2.04 Å, a little longer than the standard Ge–O covalent bond length (*ca*. 1.7–1.8 Å). (3) Four atoms, Ge1, S1, S2 and C1 are coplanar with S1, S2 and C1 in a trigonal planar arrangement around Ge. (4) The O1–Ge1–O3 hypercoordinate bond is nearly perpendicular to the S1–S2–C1 plane though the angle (166.7°) slightly deviates from the ideal trigonal bipyramidal structure.

In the case of pentacoordination of group 14 elements, deviation from the ideal trigonal bipyramidal structure is often observed. Thus, Corriu and coworkers[6] reported that the C–Si···N angle of a pentacoordinate compound, 1-(8-dimethylamino)naphthylphenylsilane, is 166.9°.

Altogether it is clear that we obtained a pentacoordinate organogermanium compound where no steric enforcement is involved to enhance the hypercoordination. It should be noted that rotation about the S–CH_2 bond, which should be feasible, would move the CO_2H group far apart from germanium. This in turn appears to suggest that the Ge–O interaction is strong enough to lead to hypercoordination. It should be noted that the solid state, trigonal bipyramidal structure of **7** can be regarded as a model for the intermediate of the S_N2 type reaction on germanium.

The ^1H and ^{13}C NMR spectra of **7** exhibit only one signal for both CH_2 protons and carbonyl carbon nuclei. This can be interpreted only if we assume a rapid equilibrium between two identical pentacoordinate species in solution as indicated below.



Notes and references

† *Crystal data* for **7**: recrystallized from AcOEt, $C_8H_{14}GeO_4S_2$, M = 310.90, monoclinic, space group *Cc*, a = 7.542(1), b = 18.100(2) c = 9.543(1) Å, β = 111.08(1)°, U = 1215.5(2) Å^3, Z = 4, T = 233 K, D_c = 1.699 Mg m^{-3}, μ = 2.855 mm^{-1}, 9790 reflectons with $2.25 \leqslant \theta \leqslant 43.50°$ were collected on a four-circle diffractometer using graphite-monochromated Mo-Kα radiation. The structure was solved using SHELXS-97 (G. M. Sheldrick, Program for Crystal Strucure Solution, University of Göttingen, Germany, 1997) and refined using SHELXL-97 (G. M. Sheldrick, Program for Crystal Strucure Solution, University of Göttingen, Germany, 1997). $R1$ = 0.034, $wR2$ = 0.0671. CCDC 182/1009

‡ Hydrogen atomic positions were calculated from assumed geometries except H4O that was located in a difference map. Hydrogen atoms were included in structure factor calculations but were not refined. The isotropic displacement parameters of the hydrogen atoms were approximated from the U_{eq} value of the atoms they were bonded to.

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