On the Hydrolysis of $tBu_2Ge(OEt)_2$: Supramolecular Self Assembly in the Solid State of 2 $tBu_2Ge(OH)_2$, $(tBu_2GeOH)_2O$, and H_2O

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Dedicated to Professor Stanislaw Pasynkiewicz on the occasion of his 70th birthday

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The hydrolysis of $tBu_2Ge(OEt)_2$ is described. Depending on the amount of water used either $tBu_2Ge(OH)_2$ (**1**) or a mixture of the latter and $(tBu_2GeOH)_2O$ (**2**) were obtained. A cocrystallate consisting of $2tBu_2Ge(OH)_2$, $(tBu_2GeOH)_2O$ and water was the subject of a single crystal X-ray diffraction study. In the solid state the individual molecules are connected by hydrogen bonds giving rise to the formation of a polymeric double chain ribbon.

Introduction

Organosilanols represent a well established class of compounds. In the solid state they are connected through hydrogen bonds and adopt various secondary structural motifs.[1] Organosilanols find applications as building blocks for the synthesis of molecular metallasiloxanes and related materials.[2] In contrast, only a very few examples of organogermanols are known, presumably because of their higher sensitivity toward self-condensation than organosilanols. For organogermanols, hydrogen bonding is also observed in the solid state.[3] As part of our ongoing studies on metallastannoxanes we prepared $tBu_2Ge(OH)_2$ by hydrolysis of $tBu_2Ge(OEt)_2$, and used this product for further investigations. Despite the mild reaction conditions applied, in one case a mixture of $tBu_2Ge(OH)_2$ and $(tBu_2GeOH)_2O$ was obtained. Attempts to separate this mixture by fractional crystallization afforded a cocrystallate of $2tBu_2Ge(OH)_2$, $(tBu_2GeOH)_2O$, and water, the structure of which is reported in this paper.

Results and Discussion

The hydrolysis of $tBu_2Ge(OEt)_2$ with a slight excess of water provided a mixture of the germanols $tBu_2Ge(OH)_2$ (**1**) and $(tBu_2GeOH)_2O$ (**2**) whereas the use of a large excess of water exclusively gave $tBu_2Ge(OH)_2$ (**1**) (Equation 1).

$$3\,tBu_2Ge(OEt)_2 \xrightarrow[\text{- EtOH}]{H_2O} \underset{\mathbf{1}}{tBu_2Ge(OH)_2} + \underset{\mathbf{2}}{(tBu_2GeOH)_2O} \qquad (1)$$

Compound **2** is the first example of a 1,1,3,3-tetraorganogermanoxane-1,3-diol. Recently, Puff et al. reported the low-yield synthesis of $tBu_2Ge(OH)_2$ (**1**) by the hydrolysis of tBu_2GeCl_2.[3a,4] Moreover, the authors used $tBu_2Ge(OH)_2$ (**1**) for the preparation of the diorganogermanium oxide *cyclo*-$(tBu_2GeO)_3$ which was obtained in moderate yield.[3a,4] However, no information was given on the identity of by-products such as **2**, or higher oligomers, from these reactions.

After the first crop of **1** had been isolated attempts to separate the above-mentioned mixture of **1** and **2** by fractional crystallisation failed. Instead, we obtained a single crystalline material which, according to ^1H NMR spectroscopy, consisted of a mixture of **1** and **2** in the ratio of 2:1. In this context it is worth mentioning that Weidenbruch et al., by the same method, succeeded in the separation of the silicon analogues $tBu_2Si(OH)_2$ and $(tBu_2SiOH)_2O$.[5]

The molecular structure of the cocrystallate is shown in Figure 1. Crystallographic data are given in Table 1 and selected bond lengths and angles are listed in Table 2.

The asymmetric unit indeed contains two molecules of **1**, a molecule of **2** and, in addition, a molecule of water; these three components are connected by a framework of hydrogen bonds (Figure 1). The mean Ge–O and Ge–C bond lengths amount to 1.77 and 1.96 Å, respectively, and are comparable with those of other organogermanols.[3] The germanium atoms of **1** and **2** show distorted tetrahedral configurations with the greatest deviations of 121.8(2) and 119.6(2)°, respectively, found for the C–Ge–C bond angles, due to the steric demand of the bulky *tert*-butyl groups. The Ge–O–Ge bond angle in **2** amounts to 143.9(2)° which is by 10.9 and 8.7° greater than the corresponding angles in $(tBu_2GeO)_3$[3a] and $(Ph_3Ge)_2O$,[6] respectively. Bearing in mind the variety of different hydrogen bonding frameworks in solid organosilanols, it is quite remarkable that the secondary structural motifs within this cocrystallate, and individual $tBu_2Ge(OH)_2$ (**1**)[3a] and $tBu_2Si(OH)_2$,[7] are virtually the same and adopt polymeric double chain ribbons (Figure 2). Selected hydrogen bond lengths and angles are listed

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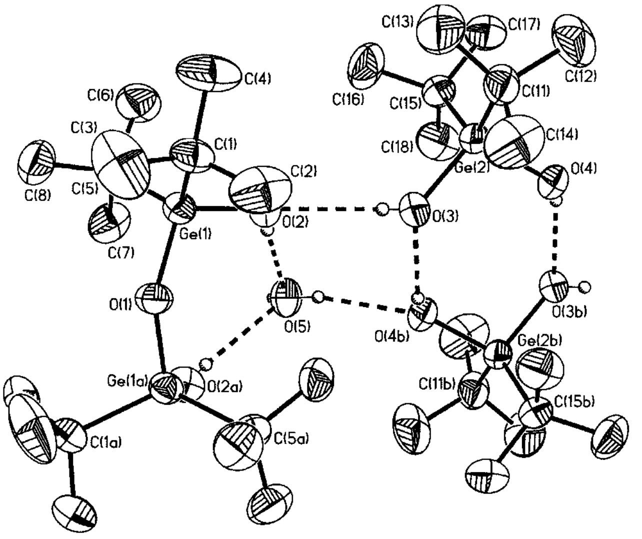

Figure 1. General view (SHELXTL-PLUS) of the cocrystallate showing 30% probability displacement ellipsoids and the atom numbering scheme

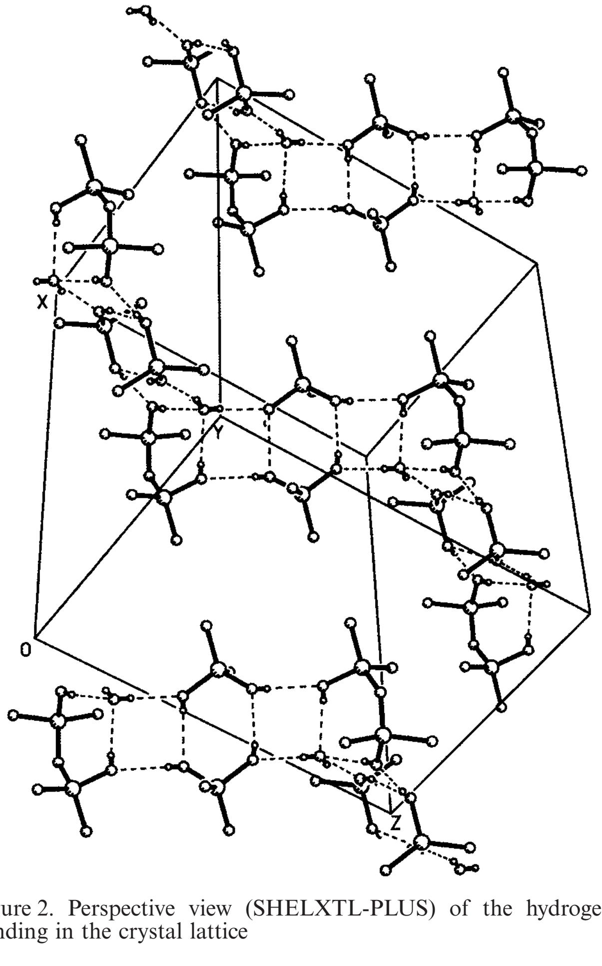

Figure 2. Perspective view (SHELXTL-PLUS) of the hydrogen bonding in the crystal lattice

Table 1. Crystal data and structure refinement for $2t\mathrm{Bu_2Ge(OH)_2\cdot(}t\mathrm{Bu_2GeOH)_2O\cdot H_2O}$

Formula	$C_{16}H_{38}Ge_2O_3\cdot 2C_8H_{20}GeO_2\cdot H_2O$
Form. wt.	883.3
Cryst. syst.	monoclinic
Cryst. size, mm	0.20 × 0.20 × 0.18
Space group	*C2/c*
a, Å	21.875(1)
b, Å	13.109(1)
c, Å	16.519(1)
β, deg	94.268(1)
V, Å^3	4723.8(5)
Z	4
ρ_{calcd}, Mg/m^3	1.242
ρ_{measd}, Mg/m^3	1.248(3)
μ, mm^{-1}	2.557
F(000)	1856
θ range, °	3.51 to 22.43
Index ranges	$-23 \leq h \leq 23$ $-14 \leq k \leq 14$ $-17 \leq l \leq 17$
No. of reflns.	23045
Completeness to θ_{max}	95.6
No. of indep. reflns./R_{int}	3071/0.0590
No. of reflns obsd with $[I > 2\sigma(I)]$	1965
No. refined params	229
GooF (F^2)	0.948
$R1$ (F) $[I > 2\sigma(I)]$	0.0321
$wR2$ ($F2$) (all data)	0.0691
$(\Delta/\sigma)_{max}$	<0.001
Largest diff peak/hole, e/Å^3	0.217/–0.283

in Table 3. The observed O···O distances in the cocrystallate are within the range of related compounds, e.g. organosilanols, and show no particularities.[1]

With the view that the crystals can be regarded as supramolecular entities, a comprehensive knowledge of the parameters which control the solid state structures is very welcome.[8] In this context it is obvious that the bulky *tert*-butyl groups dominate the structures of the above-mentioned compounds. This assumption is further supported by the isotypic di-*tert*-butyl element oxides ($t\mathrm{Bu_2MO)_3}$ (M = Si, Ge, Sn)[3a,9a,9b] and di-*tert*-butyl element imides ($t\mathrm{Bu_2MNH)_3}$ (M = Si, Sn).[10a,10b]

Experimental Section

General Remarks: $t\mathrm{Bu_2Ge(OEt)_2}$ was synthesized by the reaction of *t*BuLi with $\mathrm{Ge(OEt)_4}$.[11] – NMR spectra were recorded on a Bruker DRX 400 spectrometer operating at 400.13 MHz (^{1}H) and 100.62 MHz (^{13}C). Chemical shifts (δ) are given in ppm relative to $\mathrm{SiMe_4}$. – Mass spectra were obtained on a Finnigan MAT 8230 spectrometer. – IR spectra were recorded on a Bruker FTIR IFS 113v spectrometer. – The elemental analyses were performed on an instrument from Carlo Erba Strumentazione (Modell 1106). – The density of single crystals was determined using a Micromeritics Accu Pyc 1330.

Synthesis of Di-*tert*-butylgermane Diol (1) and 1,1,3,3-Tetra-*tert*-butyldigermanoxane-1,3-diol (2): A solution of $t\mathrm{Bu_2Ge(OEt)_2}$ (5.54 g, 20.0 mmol) in ethanol (50 mL) was treated with water (900 mg, 50.0 mmol) and heated for 15 h at 40 °C. The solvent was then removed in vacuo. The residue was recrystallized several times from chloroform at –10 °C affording colorless crystals of **1** as the first fraction (1.4 g, 6.3 mmol, 32%, m.p. 146 °C). – ^{1}H NMR (400.13 MHz, $\mathrm{CDCl_3}$): δ = 1.49 (s, 2 H, GeO*H*) 1.70 (s, 18 H, GeC*Me*$_3$). – ^{13}C{^{1}H} NMR (100.62 MHz, $\mathrm{CDCl_3}$): δ = 29.1 (Ge*C*Me$_3$) 27.4 (GeC*Me*$_3$). – IR (KBr): ν_{OH} = 3248 (bs) cm^{-1}. – $\mathrm{C_8H_{20}GeO_2}$ (220.9): C 43.50, H 9.13; found C 44.00, H 9.43. – From the residue a second crystalline fraction was obtained (2.8 g)

Table 2. Selected bond lengths [Å] and angles [°] for $2\,t\mathrm{Bu_2Ge(OH)_2}\cdot(t\mathrm{Bu_2GeOH})_2\mathrm{O}\cdot\mathrm{H_2O}$

Ge(1)–O(1)	1.7599(12)	Ge(1)–O(2)	1.779(4)
Ge(1)–C(1)	1.962(4)	Ge(1)–C(5)	1.957(4)
Ge(2)–O(3)	1.783(3)	Ge(2)–O(4)	1.772(4)
Ge(2)–C(11)	1.963(5)	Ge(2)–C(15)	1.953(4)
O(1)–Ge(1)–O(2)	109.12(18)	O(1)–Ge(1)–C(1)	105.49(17)
O(1)–Ge(1)–C(5)	109.14(13)	O(2)–Ge(1)–C(1)	105.8(2)
O(2)–Ge(1)–C(5)	107.3(2)	C(1)–Ge(1)–C(5)	119.6(2)
O(3)–Ge(2)–O(4)	103.04(18)	O(3)–Ge(2)–C(11)	108.7(2)
O(3)–Ge(2)–C(15)	108.62(17)	O(4)–Ge(2)–C(11)	103.7(2)
O(4)–Ge(2)–C(15)	109.4(2)	C(11)–Ge(2)–C(15)	121.8(2)
Ge(1)–O(1)–Ge(1a)[a]	143.9(2)		
O(2)–Ge(1)–O(1)–Ge(1a)	–28.09(17)	C(1)–Ge(1)–O(1)–Ge(1a)	–141.40(16)
C(5)–Ge(1)–O(1)–Ge(1a)	88.88(15)		

[a] Symmetry transformations used to generate equivalent atoms: *a* = –x + 1, y, –z + 0.5.

Table 3. Hydrogen bond lengths [Å] and angles [°] for $2t\mathrm{Bu_2Ge(OH)_2}\cdot(t\mathrm{Bu_2GeOH})_2\mathrm{O}\cdot\mathrm{H_2O}$

D–H···A	d (D–H)	d (H···A)	d (D···A)	(D–H–A)
O(2)–H(2')···O(5)	0.58(5)	2.27(5)	2.840(7)	173(8)
O(3)–H(3')···O(2b)[a]	0.61(4)	2.24(4)	2.849(5)	175(7)
O(4)–H(4')···O(3c)[b]	0.60(5)	2.20(5)	2.775(6)	162(8)
O(5)–H(5")···O(4)	0.65(6)	2.21(6)	2.829(4)	162(8)

[a] Symmetry transformations used to generate equivalent atoms: *b* = *x*, –*y* + 1, *z* + 0.5. – [b]Symmetry transformations used to generate equivalent atoms: *c* = –*x* + 1, –*y* + 1, –*z* + 1.

which, according to ^{1}H NMR spectroscopy, still contained a mixture of **1** and **2** in a ratio of about 2:1. From the second fraction a single crystal was taken for the X-ray diffraction studies. From the remainder, compound **2** (850 mg, 2.0 mmol, 20%, m.p. 87 °C) was isolated by size-exclusion chromatography (Sephadex-G20, $\mathrm{CH_2Cl_2}$). – ^{1}H NMR (400.13 MHz, $\mathrm{CDCl_3}$): $\delta = 1.85$ (s, 2 H, GeOH) 1.11 (s, 36 H, GeC*Me₃*). – $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (100.62 MHz, $\mathrm{CDCl_3}$): $\delta = 29.8$ (Ge*C*Me₃), 27.9 (GeC*Me₃*). – IR (KBr) ν_{OH}: 3314 (bm) $\mathrm{cm^{-1}}$. – MS; *m*/*z* (%): 367 (50) $[\mathrm{M^+} - \mathrm{C_4H_9}]$, 349 (28) $[\mathrm{M^+} - \mathrm{C_4H_{11}O}]$, 293 (72) $[\mathrm{M^+} - \mathrm{C_8H_{19}O}]$, 277 (22) $[\mathrm{M^+} - \mathrm{C_8H_{19}O_2}]$. – $\mathrm{C_{16}H_{38}Ge_2O_3}$ (423.7): C 45.35, H 9.04; found C 45.83, H 9.90. – Using the same procedure with a large excess of water (25 mL), the diorganogermane diol **1** was formed almost quantitatively.

X-ray Crystallography: Intensity data for the colorless crystals grown from chloroform were collected on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo-K_α (0.71069 Å) radiation at 291 K. The data collection covered almost the whole sphere of reciprocal space with 360 frames via ω-rotation (Δ/ω = 1°) at two times 20s per frame. The crystal-to-detector distance was 3.0 cm. Crystal decay was monitored by repeating the initial frames at the end of data collection. Analyzing the duplicate reflections there was no indication for any decay. The data were not corrected for absorption effects. The structure was solved by direct methods SHELXS97[12a] and successive difference-Fourier syntheses. Refinement applied full-matrix least-squares methods SHELXL97.[12b] – The H atoms of the hydroxy groups and the water molecule were located in the difference Fourier map and refined isotropically. The other H atoms were placed in geometrically calculated positions using a riding model (including free rotation about C–C) and refined with a common isotropic temperature factor [$\mathrm{C–H_{prim.}}$ 0.96 Å; U_{iso} 0.160(4) $\mathrm{Å^2}$]. – Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from the International Tables for X-ray Crystallography.[12c] The figures were created by SHELXTL-Plus.[12d] Crystallographic data are given in Table 1, selected bond distances and angles in Table 2, and hydrogen bond distances and angles in Table 3. – Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-136796. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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