Experimental Section

Lithium powder (0.100 g, 14.4 mmol) was added to a solution of **2** (1.23 g, 1.28 mmol) in DME (70 mL). The initially black mixture turned red and was stirred for five hours at room temperature. Insoluble compounds were filtered off and the solution was treated with 1-bromo-2,4,6-triisopropylbenzene (0.220 g, 0.78 mmol) at $-18\,^{\circ}C$. Over a period of ten hours the solution was slowly warmed to room temperature. DME was removed and the precipitate was dissolved in *n*-hexane (10 mL). Renewed filtration, concentration to a volume of 3 mL, and cooling to $-30\,^{\circ}C$ afforded greenish-black crystals of **6** (0.103 g; 11 % yield). M.p. 175–182 °C. ^1H NMR (500 MHz, $[D_8]THF$, 25 °C): $\delta = 0.02-0.10$ (m, 6H), 0.19 (d, 6H, $J = 6.6$ Hz), 0.29 (d, 6H, $J = 6.6$ Hz), 0.35 (d, 6H, $J = 6.6$ Hz), 1.05–1.17 (m, 48H), 1.21 (d, 12H, $J = 6.6$ Hz), 1.42 (d, 6H, $J = 6.6$ Hz), 1.51 (d, 6H, $J = 6.6$ Hz), 1.56 (d, 6H, $J = 6.6$ Hz), 1.60 (d, 6H, $J = 6.6$ Hz), 2.70 (sept, 4H), 2.75 (sept, 2H), 2.84 (sept, 2H), 3.09 (sept, 2H), 3.24 (sept, 2H), 3.35 (sept, 2H), 4.11 (sept, 2H), 4.27 (sept, 2H), 6.55 (s, 2H), 6.76 (s, 2H), 6.78 (s, 2H), 6.80 (s, 2H), 6.94 (s, 2H), 7.11 (s, 2H); ^{13}C NMR (125 MHz, $[D_8]THF$, 25 °C): $\delta = 14.39$, 23.49, 23.93, 24.11, 24.20, 24.28, 24.36, 24.51, 27.07, 32.51, 32.51, 34.99, 35.04, 35.27, 35.39, 37.99, 39.93, 122.14, 122.33, 122.64, 122.76, 123.52, 123.69, 142.00, 144.52, 148.05, 149.41, 150.47, 151.21, 152,45, 153.58, 154.12, 154.59; UV/Vis (*n*-hexane): $\lambda_{max}(\varepsilon) = 405$ (10450), 560 (12750) nm; C,H analysis: calcd: C 71.56, H 9.21; found: C 71.30, H 9.03.

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[8] Crystal structure analyses: Stoe-IPDS area detector, $Mo_{K\alpha}$ radiation, graphite-monochromator; $T = 193(2)$ K. The structures were solved by direct methods and refined by full-matrix least-squares techniques against F^2.[9] Hydrogen atoms were placed in calculated positions and refined with isotropic temperature factors; all other atoms were refined anisotropically. **6**: $C_{90}H_{138}Ge_4 \cdot DME$, triclinic, space group $P\bar{1}$, $a = 1576.46(7)$, $b = 1579.47(5)$, $c = 1991.89(6)$ pm, $\alpha = 78.570(4)$, $\beta = 72.713(4)$, $\gamma = 79.400(5)^{\circ}$, $Z = 2$, $V = 4600.2(3) \times 10^6$ pm^3, $\rho_{calcd} = 1.155$ g cm^{-3}, $2\theta_{max} = 52^{\circ}$. Of 56147 measured reflections, 16544 were independent, and 10596 observed for $I > 2\sigma(I)$. $R1 = 0.0460$, $wR2 = 0.1007$ (all data) for 901 parameters. **3**: $C_{87}H_{145}Ge_4LiO_6$, monoclinic, space group $C2/c$, $a = 2116.74(5)$, $b = 1800.15(7)$, $c = 2537.82(6)$ pm, $\beta = 113.395(2)^{\circ}$, $Z = 4$, $V = 8875.2(5) \times 10^6$ pm^3, $\rho_{calcd} = 1.186$ g cm^{-3}, $2\theta_{max} = 52^{\circ}$. Of 32739 measured reflections, 8135 were independent, and 4949 observed for $I > 2\sigma(I)$. $R1 = 0.0538$, $wR2 = 0.1553$ (all data) for 429 parameters. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-145476 (**6**) and CCDC-145477 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Functionalized Tellurium(II) Thiolates: Tellurium Bis(2-hydroxyethanethiolate) Hydrate, the First H_2O-Te^{II} Complex[**]

Holger Fleischer[*] and Dieter Schollmeyer

Tellurium(II) thiolates, $Te(SR)_2$ (R = alkyl, aryl) are of both chemical[1–5] and biochemical[6] interest. Thiolates $Te(SR)_2$, in which R contains a functional group, have not yet been described, despite their potential interest for synthetic and structural chemistry, for example the synthesis of precursors for the production of HgTe or CdTe semiconductors by chemical vapor deposition (CVD). We report here the synthesis of the first representative of this class of compounds and the crystal structure of its monohydrate.

Reaction of TeO_2 with $HOCH_2CH_2SH$ yields $Te(SCH_2CH_2OH)_2$ by a reductive elimination according to Equation (1).[7] With exclusion of light, solutions of $Te(SCH_2CH_2OH)_2$ in $CDCl_3$ are stable at room temperature for several days. On the other hand, ^1H NMR spectroscopy reveals rapid decomposition and the formation of Te and $(SCH_2CH_2OH)_2$, when such a solution is irradtiated with UV light ($\lambda = 254$ nm). The decomposition obeys first-order kinetics, suggesting a monomolecular mechanism for the photolysis. Preliminary results show that the OH groups of $Te(SCH_2CH_2OH)_2$ can be acetylated, and a more comprehensive account of its chemistry will be published in due course.

$$TeO_2 + 4\,HSCH_2CH_2OH \rightarrow Te(SCH_2CH_2OH)_2 + (SCH_2CH_2OH)_2 + 2\,H_2O \quad (1)$$

The complex $Te(SCH_2CH_2OH)_2 \cdot H_2O$ was obtained at $-45\,^{\circ}C$ from an ethanolic solution of $Te(SCH_2CH_2OH)_2$ containing traces of water.[8] The $Te \cdots O$ distance (249.5(10) pm) is in the range of known intramolecular dative $O \rightarrow Te$ interactions, for example 223.7(8) pm in 2-benzamidyl(bromo)tellurium,[11] and 324.4(2) pm in 4-methoxyphenyl-(*O*-methylxanthogenato)tellurium.[12] The sum of the bond angles at the tellurium center is approximately 310°; thus, the configuration of the three-coordinate Te atom can be described as distorted trigonal pyramidal. In the solid state, $Te(SCH_2CH_2OH)_2$ molecules form chains through $O3-H3 \cdots O6'$ hydrogen bonds (Figure 1); the structural parameters of the hydrogen bond are similar to those in ice.[13] Adjacent chains are linked through short $O-H \cdots S$ hydrogen bonds (cf reference [13]).

The strong intermolecular interactions lead to significant differences between the molecular structure of $Te(SCH_2CH_2OH)_2 \cdot H_2O$ optimized by ab initio methods and its structure in the crystal. In particular, the Te–O bond

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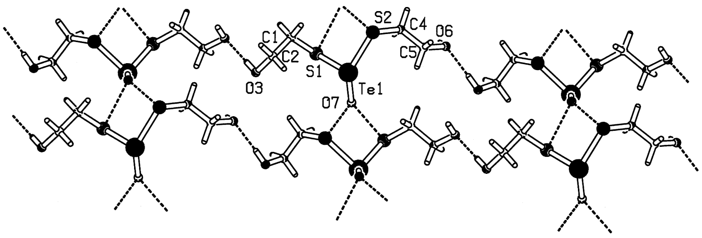

Figure 1. Packing diagram of $Te(SCH_2CH_2OH)_2 \cdot H_2O$ in the crystal. Selected distances [pm] and angles [°]: Te1-S1 239.4(3), Te1-S2 240.1(3), Te1-O7 249.5(10), S1-C1 179.9(12), S2-C4 181.5(12), C1-C2 149.9(17), C4-C5 149.2(18), C2-O3 143.4(17), C5-O6 142.8(14), O3-O6′ 276.2(12), O7-S1′ 277.4(14), O7-S2′ 252.2(15); S1-Te1-S2 101.3(1), S1-Te1-O7 75.2(3), S2-Te1-O7 133.0(3), Te1-S1-C1 103.8(4), Te1-S2-C4 104.5(4), S1-C1-C2 114.6(8), S2-C4-C5 111.3(8) C1-C2-O3 113.6(10), C4-C5-O6 113.0(10), O3-H3-O6′ 174.6; O7-Te1-S1-C1 152.9(5), O7-Te1-S2-C4 −8.6(6), C1-S1-Te1-S2 −75.4(4), C4-S2-Te1-S1 −88.8(4), C2-C1-S1-Te1 −72.2(8), C5-C4-S2-Te1 −81.6(8), O3-C2-C1-S1 −63.9(12), O6-C5-C4-S2 178.9(8).

(249.5(10) pm), which arises mainly from an n(O)-σ*(Te−S) interaction (32.8 kJ mol^{-1}), is significantly longer in the isolated molecule (296.4 pm) than in the solid state structure. The ^{1}H NMR chemical shifts of the OCH_2 and SCH_2 groups of $Te(SCH_2CH_2OH)_2 \cdot H_2O$ correspond to those of $Te(SCH_2CH_2OH)_2$, which suggests complete dissociation of the adduct in $CDCl_3$ solution. The absolute values of the S-Te-S-C torsion angles are close to 90° (calculated: 75.1 and 81.1°), as was found for other $Te(SR)_2$ compounds;[4] this may be attributed to strong hyperconjugative $(n_p)S^1$-σ(Te-S^2) interactions (69.3 kJ mol^{-1}).

Experimental Section and Computational Methods

NMR: Bruker DRX 400, 25 °C, $B_1(^1H) = 400.0$, $B_1(^{125}Te) = 126.387$ MHz; standards: TMS (^{1}H) and $Te(CH_3)_2$ (^{125}Te). IR: Mattson Galaxy 2030 FTIR, resolution 4 cm^{-1}, CsI pellet, 4000–200 cm^{-1}.

$Te(SCH_2CH_2OH)_2$: $HSCH_2CH_2OH$ (10.24 g, 131.1 mmol) and TeO_2 (5.00 g, 31.4 mmol) were suspended in methanol (40 mL) and concentrated HCl (0.2 mL) was added. The suspension was stirred in the dark for 60 h at room temperature and then filtered. The solid residue was washed several times with methanol, and the combined filtrates were concentrated and kept for two days at −45 °C. $Te(SCH_2CH_2OH)_2$ precipitated as a yellow-orange solid. Yield: 5.32 g (60.1 %). M.p. 58–60 °C (decomp). Elemental analysis (%; $C_4H_{10}O_2S_2Te$, $M = 281.84$ g mol^{-1}): calcd: C 17.05, H 3.58; S 22.75; found: C 17.06, H 3.48, S 22.41; ^{1}H NMR ($CDCl_3$): $\delta = 3.84$ (t, $^3J(H,H) = 5.6$ Hz, 2H; OCH_2); 3.33 (t, $^3J(H,H) = 5.6$ Hz, 2H; SCH_2); 2.30 (br., 1H; OH); ^{125}Te NMR ($CDCl_3$): $\delta = 1234.2$; IR: $\tilde{\nu} = 3275$ vs (ν(O−H)), 2909 s (ν(C−H)), 2858 s (ν(C−H)), 1465 s (δ(CH_2)), 1403 s (δ(CH_2)), 1013 vs (ν(C−O)), 726 (ν(S−C)), 417 m (ν(Te−S)), 335 s (ν(TeS_2)).

The ab initio calculations were performed on various servers of the Zentrum für Datenverarbeitung, Universität Mainz, using the GAUSSIAN94 software package.[15, 16]

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