

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-trisopropylbenzene (0.220 g, 0.78 mmol) at -18°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°C afforded greenish-black crystals of **6** (0.103 g; 11% yield). M.p. $175-182^{\circ}\text{C}$. ^1H NMR (500 MHz, $[\text{D}_8]\text{THF}$, 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, $[\text{D}_8]\text{THF}$, 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): $\lambda_{\text{max}}(\epsilon) = 405$ (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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Functionalized Tellurium(II) Thiolates: Tellurium Bis(2-hydroxyethanethiolate) Hydrate, the First $\text{H}_2\text{O}-\text{Te}^{\text{II}}$ Complex**

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Tellurium(II) thiolates, $\text{Te}(\text{SR})_2$ ($\text{R} = \text{alkyl, aryl}$) are of both chemical^[1–5] and biochemical^[6] interest. Thiolates $\text{Te}(\text{SR})_2$, 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 $\text{HOCH}_2\text{CH}_2\text{SH}$ yields $\text{Te}(\text{SCH}_2\text{CH}_2\text{OH})_2$ by a reductive elimination according to Equation (1).^[7] With exclusion of light, solutions of $\text{Te}(\text{SCH}_2\text{CH}_2\text{OH})_2$ 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 $(\text{SCH}_2\text{CH}_2\text{OH})_2$, when such a solution is irradiated 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 $\text{Te}(\text{SCH}_2\text{CH}_2\text{OH})_2$ can be acetylated, and a more comprehensive account of its chemistry will be published in due course.



The complex $\text{Te}(\text{SCH}_2\text{CH}_2\text{OH})_2 \cdot \text{H}_2\text{O}$ was obtained at -45°C from an ethanolic solution of $\text{Te}(\text{SCH}_2\text{CH}_2\text{OH})_2$ containing traces of water.^[8] The $\text{Te} \cdots \text{O}$ distance (249.5(10) pm) is in the range of known intramolecular dative $\text{O} \rightarrow \text{Te}$ interactions, for example 223.7(8) pm in 2-benzamidyldibromotellurium,^[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, $\text{Te}(\text{SCH}_2\text{CH}_2\text{OH})_2$ molecules form chains through $\text{O}3-\text{H}3 \cdots \text{O}6'$ hydrogen bonds (Figure 1); the structural parameters of the hydrogen bond are similar to those in ice.^[13] Adjacent chains are linked through short $\text{O}-\text{H} \cdots \text{S}$ hydrogen bonds (cf reference [13]).

The strong intermolecular interactions lead to significant differences between the molecular structure of $\text{Te}(\text{SCH}_2\text{CH}_2\text{OH})_2 \cdot \text{H}_2\text{O}$ optimized by ab initio methods and its structure in the crystal. In particular, the $\text{Te}-\text{O}$ bond

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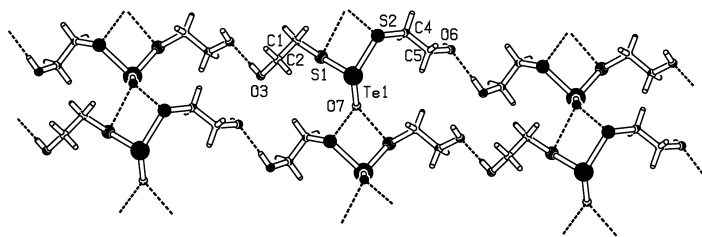


Figure 1. Packing diagram of $\text{Te}(\text{SCH}_2\text{CH}_2\text{OH})_2 \cdot \text{H}_2\text{O}$ in the crystal. Selected distances [pm] and angles [°]: Te1–S1 239.4(3), Te1–S2 240.1(3), Te1–O7 249.5(10), S1–C1 179.9(12), S2–C4 181.5(12), C1–C2 149.9(17), C4–C5 149.2(18), C2–O3 143.4(17), C5–O6 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 $n(\text{O})-\sigma^*(\text{Te}-\text{S})$ interaction (32.8 kJ mol⁻¹), is significantly longer in the isolated molecule (296.4 pm) than in the solid state structure. The ¹H NMR chemical shifts of the OCH₂ and SCH₂ groups of $\text{Te}(\text{SCH}_2\text{CH}_2\text{OH})_2 \cdot \text{H}_2\text{O}$ correspond to those of $\text{Te}(\text{SCH}_2\text{CH}_2\text{OH})_2$, which suggests complete dissociation of the adduct in CDCl₃ 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 $\text{Te}(\text{SR})_2$ compounds;^[4] this may be attributed to strong hyperconjugative (n_p)S¹– σ (Te–S²) interactions (69.3 kJ mol⁻¹).

Experimental Section and Computational Methods

NMR: Bruker DRX 400, 25 °C, $B_1(^1\text{H}) = 400.0$, $B_1(^{125}\text{Te}) = 126.387$ MHz; standards: TMS (¹H) and Te(CH₃)₂ (¹²⁵Te). IR: Mattson Galaxy 2030 FTIR, resolution 4 cm⁻¹, CsI pellet, 4000–200 cm⁻¹.

$\text{Te}(\text{SCH}_2\text{CH}_2\text{OH})_2$: HSCH₂CH₂OH (10.24 g, 131.1 mmol) and TeO₂ (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. $\text{Te}(\text{SCH}_2\text{CH}_2\text{OH})_2$ precipitated as a yellow-orange solid. Yield: 5.32 g (60.1 %). M.p. 58–60 °C (decomp). Elemental analysis (%): C₄H₁₀O₂S₂Te, $M = 281.84$ g mol⁻¹; calcd: C 17.05, H 3.58; S 22.75; found: C 17.06, H 3.48, S 22.41; ¹H NMR (CDCl₃): $\delta = 3.84$ (t, ³J(H,H) = 5.6 Hz, 2H; OCH₂); 3.33 (t, ³J(H,H) = 5.6 Hz, 2H; SCH₂); 2.30 (br., 1H; OH); ¹²⁵Te NMR (CDCl₃): $\delta = 1234.2$; IR: $\tilde{\nu} = 3275$ vs ($\nu(\text{O}-\text{H})$), 2909 s ($\nu(\text{C}-\text{H})$), 2858 s ($\nu(\text{C}-\text{H})$), 1465 s ($\delta(\text{CH}_2)$), 1403 s ($\delta(\text{CH}_2)$), 1013 vs ($\nu(\text{C}-\text{O})$), 726 ($\nu(\text{S}-\text{C})$), 417 m ($\nu(\text{Te}-\text{S})$), 335 s ($\nu(\text{TeS}_2)$).

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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