Nucleophilic Addition of Telluroxides to a Cationic Ditelluroxane: Oligotelluroxanes[**]

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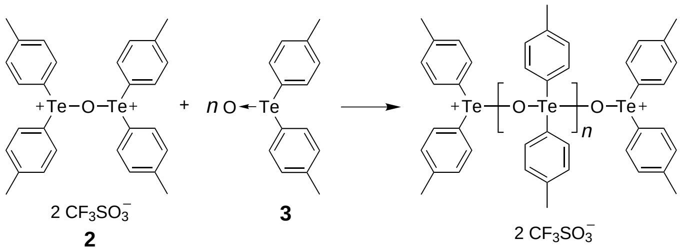
Linear polymers with oxo bridges between main group elements or transition metals, such as siloxanes and titanoxanes, have attracted considerable attention with regard to materials science.[1] Polytelluroxanes $XPh_2Te[OTePh_2]_nO\text{-}TePh_2X$ (**1**), in which tellurium units are linked by oxo bridges and possess a hypervalent bonding character,[2–4] have not been extensively explored, because a general method for their synthesis was not available. Ditelluroxanes **1** ($n = 0$) were synthesized by the thermal dehydration of diaryltellurium hydroxide halides and related compounds $Ar_2Te(OH)X$ (X = Cl, Br, NSC, etc.).[5] Domasevitch et al. reported the synthesis of the tritelluroxane **1** ($n = 1$, X = nitrosocarbamylcyanomethanide) by the dehydration procedure.[6, 7] In the recently reported μ-oxo-bis[bis(4-methylphenyl)tellurium(IV)] bis(trifluoromethanesulfonate) (**2**), the tellurium atoms exhibit cationic character in solution.[8] These tellurium cations can react with nucleophiles, for instance, with bis(4-methylphenyl) telluroxide (**3**), to produce oligotelluroxanes **4**. Because the terminal Te atoms in the polytelluroxanes carry a positive charge, further addition of **3** can lengthen the chain of **4**. Here we report the synthesis and characterization of the oligotelluroxanes **4** ($n = 1-4$) from the ditelluroxane **2** and the telluroxide **3** (Scheme 1).



2

3

4a: $n = 1$, **b**: $n = 2$
c: $n = 3$, **d**: $n = 4$

Scheme 1. Synthesis of **4** from **2** and n equivalents of **3**.

The reaction of the ditelluroxane **2** with n equivalents of the telluroxide **3** in dry CH_2Cl_2 at room temperature afforded the oligotelluroxanes **4** (>95% yield) as a white powder after precipitation with n-hexane. Representative results for the formation of the oligotelluroxanes are listed in Table 1. The tritelluroxane **4a**, the tetratelluroxane **4b**, and the pentatelluroxane **4c** were the only products when stoichiometric amounts of **2** and **3** reacted at room temperature in CH_2Cl_2. Four equivalents of **3** and one equivalent of **2** in CH_2Cl_2 for 72 h at room temperature gave a mixture of the penta- and the hexatelluroxane **4d** in the ratio of 2.5:1. The oligotelluroxanes **4** can be converted back to the starting material **3** quantitatively by treatment with aqueous NaOH (2 M) in CH_3CN at room temperature.

Table 1. Oligotelluroxanes **4a–d** from the ditelluroxane **2** and the telluroxide **3**.

3 [equiv]	Time [h]	Product[a] (ratio)[b]	Yield [%]
1	12	**4a**	>95
2	12	**4b**	>95
3	12	**4c**	>95
4	72	**4d** + **4c** (1:2.5)	>95

[a] **4a** = tritelluroxane, **4b** = tetratelluroxane, **4c** = pentatelluroxane, **4d** = hexatelluroxane. [b] Determined by integration of ^{125}Te NMR spectrum of the reaction mixture.

The ^{1}H NMR spectra of **4a–d** in CD_3CN or [D$_8$]THF at room temperature exhibit one set of AA′BB′ signals for the aromatic protons, whereas two well-resolved sets of AA′BB′ signals are present for **4a** at −40 °C and for **4b** at −90 °C. For **4c** and **4d**, two sets of multiplets are observed at −90 °C. Well-resolved sharp peaks in the ^{125}Te NMR spectra appear at −40 °C for **4a** and at −90 °C for **4b–d**.[9]

The ^{125}Te NMR chemical shifts and integration ratios of **4a–d** are summarized in Table 2. The signals of the terminal telluronium groups and the inner tellurane units in the backbone of **4** appear in the downfield region of $\delta = 1312-1224$[8] and in the upfield region of δ 1125–990,[10] respectively. Chemical shifts of both the telluronium and tellurane moieties are shifted upfield with increasing degree of oligomerization. This distinctive change in chemical shift strongly suggests that the cationic character of the terminal telluronium moieties in **4** becomes less pronounced with increasing degree of oligomerization. Therefore, the reactivity of **4** with respect to **3** decreases in the order **4a** > **4b** > **4c** > **4d**. The competitive reaction of a 1:1 mixture of the tritelluroxane **4a** and the tetratelluroxane **4b** with one equivalent of **3** afforded **4b** as the sole product (Scheme 2). Thus, the degree of oligomerization can be controlled by means of the ratio of **3** to **2**.

Table 2. ^{125}Te NMR chemical shifts and integration ratios of **4a–d**.[a]

Telluroxane	δ	Ratio
2[8]	1288.4	
4a	1311.9, 1124.7	2:1
4b	1263.4, 1063.4	2:2
4c	1242.2, 1087.0, 992.9	2:2:1
4d	1224.2, 1096.2, 990.1	2:2:2

[a] Measured in CD_3CN at −40 °C for **2** and **4a** and in [D$_8$]THF at −90 °C for **4b–d**.

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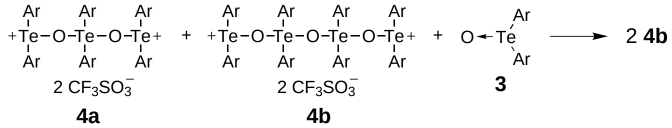

Scheme 2. Competitive reaction of a 1:1 mixture of **4a** and **4b** with one equivalent of **3**.

The molecular and electronic structure of oligotelluroxanes was evaluated for model compounds **5a**–**d**[11] by B3LYP DFT calculations.[12, 13] The geometries of **5a**–**d** optimized in C_{2v} symmetry with a zigzag skeletal structure (Figure 1).[14] The atomic charges of the Te atoms and the LUMO energies are listed in Table 3.[15] The positive charge on the terminal Te atoms decreases slightly with increasing degree of oligomerization. In all compounds, the LUMO is delocalized along the Te–O backbone and has antibonding character between adjacent Te and O atoms. This could be a reflection of the fact that the backbone of strongly polarized Te–O bonds is a delocalized σ-electron system. The energy of the LUMO increases in the order **5a** < **5b** < **5c** < **5d**. The calculated energy changes for formation of **5b** from **5a** and dimethyl telluroxide, **5c** from **5b**, and **5d** from **5c** are −74.2, −48.9, and −37.5 kcal mol^{-1}, respectively. These results explain the reactivity trends of the telluroxanes **2** and **4a**–**d**.

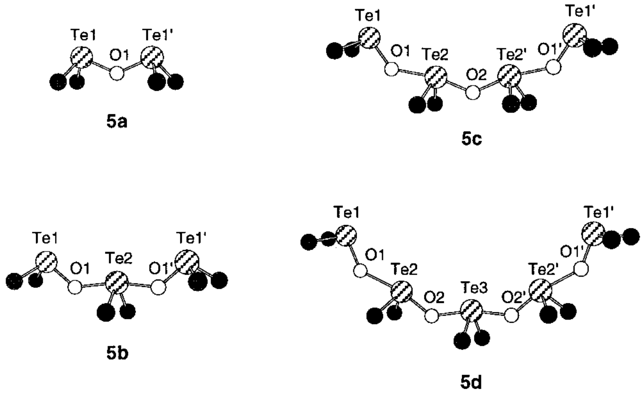

Figure 1. Optimized C_{2v} structures of oligotelluroxanes **5a**–**d**; hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: **5a**: Te1–O1 1.964; Te1-O1-Te1′ 133.0. **5b**: Te1–O1 1.895, O1–Te2 2.133; Te1-O1-Te2 134.3, O1-Te2-O1′ 168.1. **5c**: Te1–O1 1.868, O1–Te2 2.263, Te2–O2 1.999; Te1-O1-Te2 136.4, O1-Te2-O2 168.0, Te2-O2-Te2′ 134.8. **5d**: Te1–O1 1.854, O1–Te2 2.363, Te2–O2 1.943, O2–Te3 2.090; Te1-O1-Te2 138.6, O1-Te2-O2 168.6, Te2-O2-Te3 135.7, O2-Te3-O2′ 167.0.

Table 3. Atomic charges on the Te atoms and the energy of the LUMO in the model compounds **5a**–**d**.

Telluroxane	Atomic charge			LUMO
	Te1	Te2	Te3	[eV]
5a	+1.860			−11.36
5b	+1.847	+1.861		−8.64
5c	+1.841	+1.873		−7.11
5d	+1.838	+1.878	+1.885	−6.15

Slow diffusion of *n*-hexane into a solution of a mixture of **4a** and **2** in ethyl acetate gave single crystals of the 1:1 complex of **4a** and **2**, the crystal structure of which was determined by X-ray diffraction analysis (Figure 2).[16] In the **4a** unit, the terminal atoms Te1 and Te3 and the central atom Te2 form a telluronium and a tellurane moiety, respectively. Assembly of **4a** and **2** by interaction of their terminal Te atoms with two counterions affords a 14-membered pseudoring with interatomic Te···O distances in the range of 2.55–2.79 Å. All the atoms of this ring are nearly coplanar. The other two counterions are accommodated in the cavity of the macrocycle.

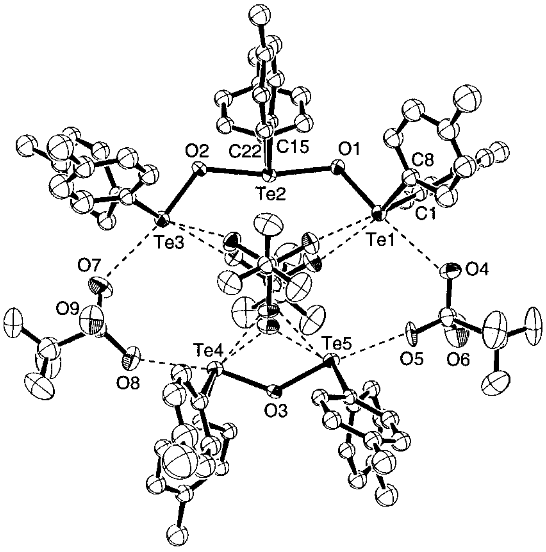

Figure 2. ORTEP plot of the 1:1 complex of **4a** and **2** (15% probability thermal ellipsoids); hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Te1–O1 1.890(8), Te2–O1 2.089(8), Te2–O2 2.116(8), Te3–O2 1.896(8), Te4–O3 1.916(8), Te5–O3 1.964(7), Te1···O4 2.79(1), Te3···O7 2.76(1), Te4···O8 2.55(1), Te5···O5 2.555(9); Te1-O1-Te2 125.3(4), Te2-O2-Te3 122.0(4), Te4-O3-Te5 131.0(4), O1-Te1-C1 93.5(4), O1-Te1-C8 93.3(5), C1-Te1-C8 98.0(5), O1-Te2-O2 167.8(3), O1-Te2-C15 84.8(4), O1-Te2-C22 89.1(4), C15-Te2-C22 97.5(5), O1-Te1···O4 170.7(4), O2-Te3···O7 173.2(4), O3-Te4···O8 166.5(4), O3-Te5···O5 169.2(4).

We have demonstrated the selective formation of the cationic oligotelluroxanes **4** by reaction of the ditelluroxane **2** as initiator with the diaryl telluroxide **3** as monomer under mild conditions. Studies on the extension of this reaction to polytelluroxanes and the application of **4** as a building block for molecular assembly[17] are underway.

Experimental Section

4: To a mixture of **2** (100.0 mg, 0.107 mmol) and *n* equivalents of **3** ($n \times 34.9$ mg, $n \times 0.107$ mmol; $n = 1$–4) under an argon atmosphere was added dry CH_2Cl_2 (2 mL) at room temperature. The resulting solution was stirred for 12 h at room temperature and then poured into *n*-hexane (50 mL) to precipitate the oligotelluroxane **4** (> 95% yield) as a white powder.

4a: M.p. 216–218 °C (decomp); ^{1}H NMR (270 MHz, CD_3CN, −40 °C): δ = 2.33 (s, 6H), 2.34 (s, 12H), 7.14, 7.47 (AA′BB′, J = 8.1 Hz, 8H), 7.27, 7.44 (AA′BB′, J = 8.6 Hz, 16H); ^{125}Te NMR (85.2 MHz, CD_3CN, −40 °C): δ = 1124.7, 1311.9 (integration ratio 1:2); FAB-MS: *m/z* (%): 1111 (13) $[M - CF_3SO_3]^+$, 785 (39) $[M - \mathbf{3} - CF_3SO_3]^+$, 329 (58) $[\mathbf{3}+H]^+$, 312 (100) $[\mathbf{3} - O]^+$; elemental analysis calcd for $C_{44}H_{42}F_6O_8S_2Te_3 \cdot H_2O$ (%): C 41.36, H 3.47; found: C 41.09, H 3.37.

4b: M.p. 98–100 °C (decomp); ^{1}H NMR (270 MHz, [D$_8$]THF, −90 °C): δ = 2.30 (s, 12H), 2.32 (s, 12H), 7.18, 7.74 (AA′BB′, J = 8.4 Hz, 16H), 7.25, 7.67 (AA′BB′, J = 8.4 Hz, 16H); ^{125}Te NMR (85.2 MHz, [D$_8$]THF, −90 °C): δ = 1063.4, 1263.4 (integration ratio 1:1); FAB-MS: m/z (%): 1437 (2) [$M - CF_3SO_3$]$^+$, 1111 (36) [M − **3** − CF_3SO_3]$^+$, 785 (64) [M − 2**3** − CF_3SO_3]$^+$, 329 (71) [**3**+H]$^+$, 312 (100) [**3** − O]$^+$; elemental analysis calcd for $C_{58}H_{56}F_6O_9S_2Te_4 \cdot H_2O$ (%): C 43.44, H 3.65; found: C 43.25, H 3.50.

4c: M.p. 94–97 °C (decomp); ^{1}H NMR (270 MHz, [D$_8$]THF, −90 °C): δ = 2.24 (s, 12H), 2.28 (s, 12H), 2.32 (s, 6H), 7.05–7.35 (m, 20H), 7.58–7.88 (m, 20H); ^{125}Te NMR (85.2 MHz, [D$_8$]THF, −90 °C): δ = 992.9, 1087.0, 1242.2 (integration ratio 1:2:2); FAB-MS: m/z (%): 1437 (1.4) [M − **3** − CF_3SO_3]$^+$, 1111 (15) [M − 2**3** − CF_3SO_3]$^+$, 785 (36) [M − 3**3** − CF_3SO_3]$^+$, 329 (76) [**3**+H]$^+$, 312 (100) [**3** − O]$^+$; elemental analysis calcd for $C_{72}H_{70}F_6O_{10}S_2Te_5 \cdot H_2O$ (%): C 44.82, H 3.76; found: C 44.87, H 3.69.

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Synthesis and Characterization of a Unimolecular Capsule**

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Host molecules that completely surround other molecules make use of either strong covalent bonds as in carcerands[1] and cryptophanes, [2] or weak hydrogen bonds as in self-assembling capsules.[3] The former type offers the kinetic stability needed to isolate reactive intermediates[4] and restrict molecular motions,[5] while the latter type shows the dynamic lability useful in recognition[6] and catalysis.[7] We describe

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