Telluronic Acids

DOI: 10.1002/anie.201002545

A Well-Defined Dinuclear Telluronic Acid $[RTe(\mu\text{-}O)(OH)_3]_2$**

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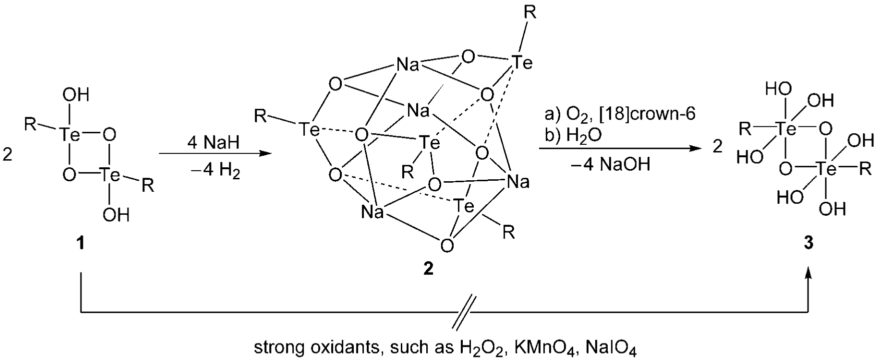
In memory of Herbert Schumann

Compared to the well-established chemistry of sulfonic acids, RSO_3H, and their extensive utility in organic synthesis, the knowledge of the heavier congeners is rather modest. This discrepancy is arguably due to their tedious preparation and difficult handling.[1–4] Like sulfonic acids, selenonic acids, $RSeO_3H$,[1] are strong acids. However, unlike their sulfur analogues, selenonic acids are also strong oxidizing reagents; sufficiently strong to oxidize chloride ions to chlorine.[2] Although benzeneselenonic acid, $PhSeO_3H$, was obtained by selenonation of benzene,[3] a more general route for the preparation of selenonic acids, $RSeO_3H$, involves the oxidation of readily available seleninic acids, $RSeO_2H$, by $KMnO_4$ to give the potassium selenates $K[RSeO_3]$, which upon treatment with $HClO_4$ liberate the free acids.[4] Selenonic acids, $RSeO_3H$, are thermally unstable. Concentrated solutions of trifluoromethaneselenonic acid, F_3CSeO_3H, the selenium analogue of triflic acid, decompose violently at ambient temperature.



Scheme 1. Synthesis of **2** and **3** ($R = 2,6\text{-}Mes_2C_6H_3$).

Progress in the synthesis of stable hexacoordinate organotellurium(VI) compounds, such as R_6Te, Ph_5TeF, and R_4TeF_2 ($R = Me, Ph$)[5] prompted us to investigate the preparation of hitherto unknown telluronic acids, which was achieved for a kinetically stabilized prototype in two simple preparative steps (Scheme 1).

The dinuclear *m*-terphenyltellurinic acid $[2,6\text{-}Mes_2C_6H_3Te(\mu\text{-}O)(OH)]_2$[6] (**1**) was treated with sodium hydride to give the tetranuclear sodium *m*-terphenyltellurinate $Na_4(2,6\text{-}Mes_2C_6H_3Te)_4(\mu_3\text{-}O)_8$ (**2**), which was oxidized by dry O_2 in the presence of [18]crown-6 to afford the dinuclear *m*-terphenyltelluronic acid $[2,6\text{-}Mes_2C_6H_3Te(\mu\text{-}O)(OH)_3]_2$ (**3**). In the absence of crown ether no reaction took place. It should also be noted that all attempts to prepare **3** by the direct oxidation of **1** using various strong oxidants, such as H_2O_2, $KMnO_4$, or $NaIO_4$, failed.

The molecular structure of **2** comprises an unprecedented $Na_4Te_4O_8$ cage structure that is completely shielded by four *m*-terphenyl groups (Figure 1).[7] The spatial arrangement of the crystallographically equivalent Te atoms of **2** is distorted tetrahedral when taking into account the primary coordination sphere (O_2C donor set) and the stereochemically active lone pair. The Te–O bond lengths of 1.832(4) and 1.850(4) Å are significantly shorter than the average 'standard Te–O single bonds' of $[(4\text{-}MeOC_6H_4)_2TeO]_n$ (2.063(2) Å)[8] and indicate a formal bond order of 1.5. The coordination of the

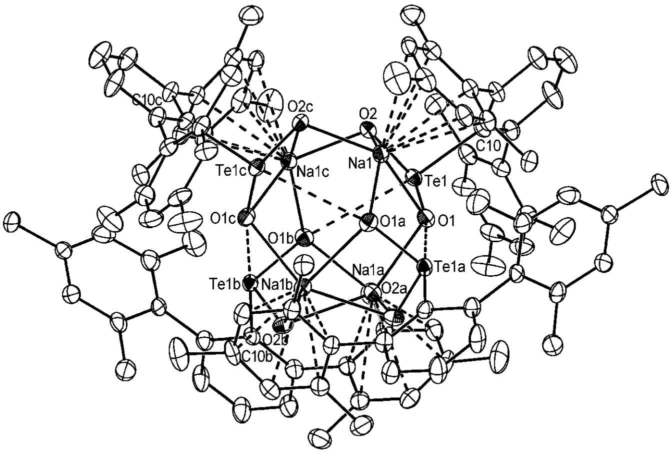


Figure 1. Molecular structure of **2**; thermal ellipsoids are set at 30% probability. Selected interatomic distances [Å]: Te1–O1 1.850(4), Te1···O1b 3.195(4), Te1–O2 1.832(4), Te1–C10 2.163(5), Na1–O1 2.568(5), Na1–O1a 2.357(4), Na1–O2 2.469(5), Na1–O2c 2.261(4).

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[**] $R = 2,6\text{-}Mes_2C_6H_3$. The Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged for financial support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201002545.

Te atoms is completed by a secondary Te···O contact of 3.195(4) Å, that is substantially shorter than the sum of van der Waals radii (3.5 Å).[9]

The spatial arrangement of the sodium atoms is square pyramidal and defined by four Na–O bonds ranging from 2.261(4) to 2.568(5) Å as well as the η^6-coordination with one of the mesityl group of the organic substituent (shortest distance from the ideal plane 1.703(4) Å). Of note is that **2** is a potential model compound for amorphous sodium tellurite glasses $(Na_2O)_x(TeO_2)_{1-x}$ $(0.10 < x < 0.35)$, for which little structural information is available.[10] In solution, **2** is characterized by a ^{125}Te NMR spectroscopic chemical shift of $\delta = 1698$ ppm, which is significantly different from that of the parent acid **1** ($\delta = 1403$ ppm).[6]

The molecular structure of **3** comprises a dinuclear four-membered Te_2O_2 ring structure that is completely shielded by two *m*-terphenyl groups (Figure 2). The spatial arrangement of the Te atoms of **3** is octahedral and defined by an O_5C donor set. The average Te–O bond lengths of 1.938(3) Å compare well with that of cubic orthotelluronic acid $Te(OH)_6$ (1.912(6) Å).[11] The IR spectrum of **3** shows two sharp intense signals at $\tilde{\nu} = 3665$ and $3616\ cm^{-1}$, which are assigned to OH stretching vibrations. The ^{125}Te NMR spectrum ($CDCl_3$) of **3** shows one signal at $\delta = 783$ ppm.

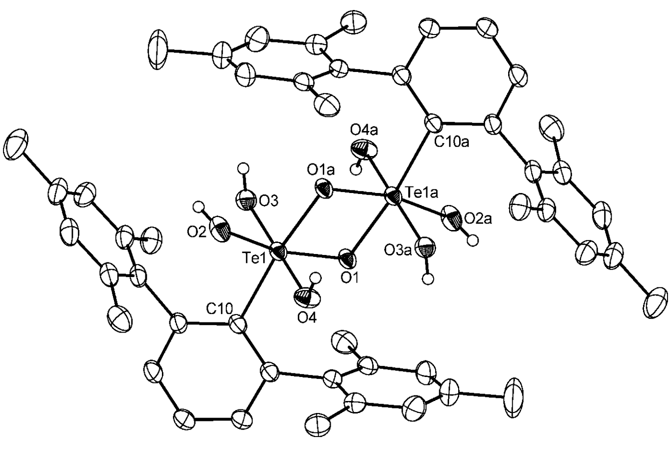

Figure 2. Molecular structure of **3**; thermal ellipsoids are set at 30% probability. Selected bond lengths [Å]: Te1–O1 1.943(2), Te1–O1a 1.971(2), Te1–O2 1.918(2), Te1–O3 1.938(3), Te1–O4 1.918(3), Te1–C10 2.154(3).

To estimate the relative stability of meta-, meso-, and orthophenylchalcogonic acids, DFT calculations were performed at the B3PW91/TZ level of theory (Figure 3).[12] These calculations confirm that for the lighter elements the tetracoordinated metaphenylchalcogonic acids $PhE(=O)_2OH$ (E = S,Se; (0 kJ mol^{-1})) are more stable than the pentacoordinated mesophenylchalcogonic acids $PhE(=O)(OH)_3$ (174 kJ mol^{-1} for E = S; 47 kJ mol^{-1} for E = Se) and the hexacoordinated orthophenylchalcogonic acids $PhE(OH)_5$ (263 kJ mol^{-1} for E = S; 46 kJ mol^{-1} for E = Se) and paraphenylchalcogonic acid $[PhE(\mu_2\text{-}O)(OH)_3]_2$ (241 kJ mol^{-1} for E = S; 33 kJ mol^{-1} for E = Se).

By contrast, the tetracoordinated metaphenyltelluronic acid $PhTe(=O)_2OH$ (173 kJ mol^{-1}) and the pentacoordinated mesophenyltelluronic acid $PhTe(=O)(OH)_3$ (101 kJ mol^{-1}) are less stable than the hexacoordinated orthophenyltelluronic acid $PhTe(OH)_5$ (3 kJ mol^{-1}) and paraphenylchalcogonic acid $[PhTe(\mu\text{-}O)(OH)_3]_2$ (0 kJ mol^{-1}), which have nearly the same stability. MP2 calculations performed at the same level of theory confirm the same trend; however, the energy differences are slightly more pronounced than for the DFT calculations (Figure 3).

Both the experimental and computational results uniformly show that a qualitative change in structures of arylchalcogonic acids occurs when going from 4th to the 5th period. We are currently investigating the reactivity of **3** and related compounds.

Experimental Section

2: A mixture of **1** (1.00 g, 1.10 mmol) and NaH (56 mg, 2.3 mmol) in toluene (40 mL) was stirred for 12 h at room temperature. The solution was filtered and the solvent removed in vacuum. The solid residue was recrystallized from MeCN/THF to give colorless crystals of **2** (890 mg, 0.45 mmol, 82%).

^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.39$ (t, 1H, Ar), 6.89 (d, 2H, Ar), 6.27 (s, 4H, Ar), 2.18 (s, 6H, CH_3), 1.96 (s, 12H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 147.5$, 144.6, 137.9, 137.6, 137.0, 130.0, 129.3, 108.0 (Ar), 21.2, 21.1 (CH_3) ppm. ^{125}Te NMR ($CDCl_3$, 126 MHz): $\delta = 1698$ ppm. IR (KBr): $\tilde{\nu}_{OH} = 3665$ and $3616\ cm^{-1}$. Elemental analysis calcd (%) for $C_{96}H_{100}Na_4O_8Te_4$ (1984.16): C 58.11, H 5.08; found: C 58.49, H 5.39.

3: Oxygen was bubbled through a hot solution of **2** (800 mg, 0.40 mmol) and [18]crown-6 (422 mg, 1.6 mmol) in THF (50 mL) for 2 h. Water (5 mL) was added and the layers separated. The organic layer was dried over Na_2SO_4 and the solvent removed in vacuum. The solid residue was recrystallized from THF/hexane and the solid dried in vacuum to give **3** as colorless solid (320 mg, 0.12 mmol, 50%).

^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.43$ (t, 1H; Ar), 6.92 (d, 2H; Ar), 6.29 (s, 4H; Ar), 2.22 (s, 6H; CH_3), 1.98 ppm (s, 12H; CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 146.9$, 144.1, 137.2, 136.8, 136.0,

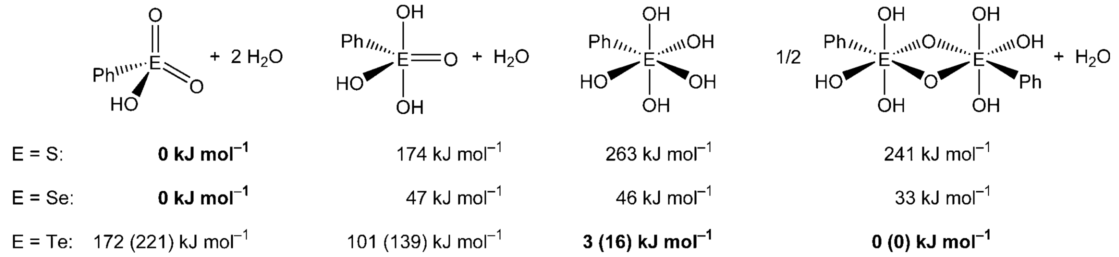

Figure 3. Relative stability of meta-, meso-, ortho-, and paraphenylchalcogonic acids (DFT/B3PW91 calculations for S, Se, and Te compounds; MP2 calculations for Te compounds in parenthesis).

129.9, 128.5, 126.9 (Ar), 20.8, 20.7 ppm (CH_3). ^{125}Te NMR ($CDCl_3$, 126 MHz): $\delta = 783$ ppm. Elemental analysis calcd (%) for $C_{48}H_{56}O_8Te_2$ (1016.23): C 56.73, H 5.55; found: C 56.49, H 5.43.

Received: April 28, 2010

Keywords: hypervalent compounds · oxides · tellurium

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[7] a) Crystal data for **2**·4 THF ($C_{112}H_{132}Na_4O_{12}Te_4$): $M_r = 2272.54$, tetragonal space group $I\bar{4}$, $a = b = 19.238(6)$, $c = 14.276(5)$ Å, $V = 5283(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.428$ mg m^{-3}, crystal dimensions $0.25 \times 0.31 \times 0.42$ mm^3. 10780 collected and 6387 unique reflections. Final residuals $R_1 = 0.0419$, $wR_2 = 0.0838$ ($I > 2\sigma(I)$); $R_1 = 0.0708$, $wR_2 = 0.0912$ (all data). GooF = 0.877, 298 parameters. CCDC 782648 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif; b) Crystal data for **3**·4 THF: ($C_{64}H_{88}O_{12}Te_2$): $M_r = 1304.54$, monoclinic space group $P2_1/n$, $a = 13.4434(9)$, $b = 15.9771(9)$, $c = 16.170(1)$ Å, $\beta = 113.191(5)°$, $V = 3192.5(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.357$ mg m^{-3}, crystal dimensions $0.5 \times 0.5 \times 0.5$ mm^3. 20749 collected and 8557 unique reflections. Final residuals $R_1 = 0.0401$, $wR_2 = 0.1113$ ($I > 2\sigma(I)$); $R_1 = 0.0572$, $wR_2 = 0.1280$ (all data). GooF = 1.055, 352 parameters. CCDC 782649 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[10] Sodium tellurite glasses $(Na_2O)_x(TeO_2)_{1-x}$ ($0.10 < x < 0.35$) are promising optical materials characterized by a high refractive index, good and wide IR transmittance, and a large third order non-linear optical susceptibility. These remarkable properties arise from the free electron pair in the structural motifs of the Te^{IV} sites. While the network builder (TeO_2) itself is only a conditional glass former, the sodium oxide modifier (Na_2O) gives rise to stable and chemically durable glasses. The modifier changes the number of TeO_4 and TeO_3 structural units and thus, the glass transition temperature and non-linear optical response; a) R. El-Mallawany, *Mater. Chem. Phys.* **1998**, *53*, 93–120; b) R. El-Mallawany, *Mater. Chem. Phys.* **1999**, *60*, 103–131; c) R. El-Mallawany, *Mater. Chem. Phys.* **2000**, *63*, 109–115; d) J. C. McLaughlin, S. L. Tagg, J. W. Zwanziger, D. R. Haeffner, S. D. Shastri, *J. Non-Cryst. Solids* **2000**, *274*, 1–8; e) J. C. McLaughlin, S. L. Tagg, J. W. Zwanziger, *J. Phys. Chem. B* **2001**, *105*, 67–75.

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[12] Calculations were performed both at the DFT/B3PW91 as well as at the MP2 level of theory. For tellurium an effective core potential with a cc-pVTZ basis set was applied, the split-valence 6-311+G(2df,p) basis set for all other atoms was used. Stationary points were characterized as true minima by frequency calculations. See Supporting Information for details.