Main-Group Chemistry

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Well-Defined Stibonic and Tellurinic Acids**

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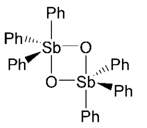
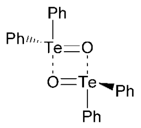
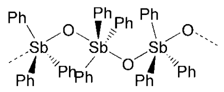
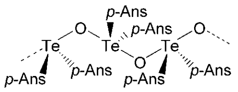
The first stibonic acids $RSb(O)(OH)_2$[1] and tellurinic acids $RTe(O)(OH)$[2] (R = aryl, alkyl) were extensively investigated more than 90 years ago in the context of pharmacological studies on arsonic acids $RAs(O)(OH)_2$ and the closely related remedies atoxyl and salvarsan, marking the beginning of modern chemotherapy.[3] Unlike their lighter Group 15 and 16 congeners, all hitherto described stibonic and tellurinic acids are ill-defined, amorphous, high-melting compounds that are poorly soluble in most organic solvents. Molecular weight determinations[4] and ^{121}Sb Mössbauer spectroscopic studies[5] confirm a high degree of aggregation and a trigonal-bipyramidal structure for $PhSb(O)(OH)_2$. By contrast, all phosphonic and arsonic acids $RE(O)(OH)_2$ (E = P, As), as well as sulfinic and seleninic acids $RE(O)(OH)$ (E = S, Se), are well-defined molecular compounds with tetrahedrally coordinated central atoms E, polar (formal) E=O double bonds and E–OH groups that are usually involved in intermolecular hydrogen bonding in the solid state.

Aggregation was also observed for related triarylantimony oxides and diaryltellurium oxides, which exist in two distinctively different structures, namely as asymmetric dimers, for example $(Ph_3SbO)_2$[6] and $(Ph_2TeO)_2$,[7] and as one-dimensional polymers, for example, $(Ph_3SbO)_n$[8] and $(p\text{-}Ans_2TeO)_n$ (Ans = $MeOC_6H_4$).[9]

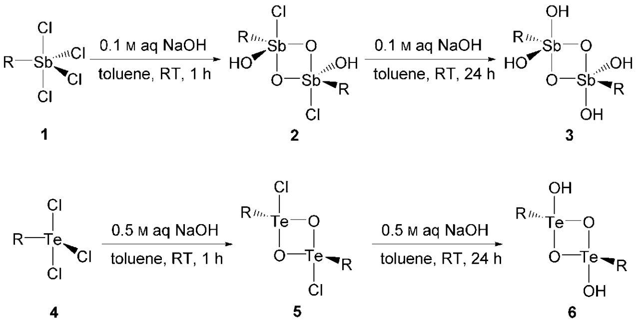








These observations prompted us to study the structures of archetypal stibonic and tellurinic acids that are kinetically stabilized by a bulky *m*-terphenyl substituent. The kinetically controlled hydrolysis under basic conditions (in a two-layer system of toluene and 0.1 M aqueous sodium hydroxide) of 2,6-$Mes_2C_6H_3SbCl_4$ (**1**; Mes = 2,4,6-$Me_3C_6H_2$) provided the μ_2-oxo-bridged dinuclear products [2,6-$Mes_2C_6H_3Sb(O)(OH)Cl]_2$ (**2**) and [2,6-$Mes_2C_6H_3Sb(O)(OH)_2]_2$ (**3**) in high yields (Scheme 1). Our recent attempts at preparing **3** by the basic hydrolysis of 2,6-$Mes_2C_6H_3SbCl_2$ under aerobic conditions gave rise to the kinetically controlled formation of (2,6-$Mes_2C_6H_3Sb^{III}Cl)_2O$ and the mixed-valent antimony oxo clusters (2,6-$Mes_2C_6H_3Sb^{V})_2(ClSb^{III})_4O_8$ and (2,6-$Mes_2C_6H_3Sb^{V})_4(ClSb^{III})_4(HOSb^{III})_2O_{14}$, which evolved from partial cleavage of Sb–C bonds.[10] Given that reaction conditions were similar in both studies, it appears that the Sb^{V}–C bonds are more resistant towards hydrolysis than the Sb^{III}–C bonds of the same *m*-terphenyl substituent.



Scheme 1. Synthesis of **2**, **3**, **5**, and **6**. R = 2,6-$Mes_2C_6H_3$.

The kinetically controlled hydrolysis of 2,6-$Mes_2C_6H_3TeCl_3$ (**4**) in a two-layer system of toluene and 0.5 M aqueous sodium hydroxide solution affords the μ_2-oxo-bridged dinuclear products [2,6-$Mes_2C_6H_3Te(O)Cl]_2$ (**5**) and [2,6-$Mes_2C_6H_3Te(O)(OH)]_2$ (**6**) in high yields (Scheme 1).

The molecular structures of **3** and **6** comprise asymmetric four-membered Sb_2O_2 and Te_2O_2 ring structures with one or two exocyclic OH groups (Figures 1 and 2).[11] Taking into account the lone pair at the tellurium center, the spatial arrangement around the Sb and Te atoms is best described as distorted trigonal-bipyramidal with the expected occupancies of the ligand atoms. The inorganic cores of **3** and **6** are effectively shielded by the bulky *m*-terphenyl substituents, which prevent further aggregation, while in **6** two mesityl groups in *ortho* position are engaged in Menshutkin type interactions with the lone pairs of the Te atoms (centroid (C20–C25)···Te1 3.399(1) Å).[12] In **3** the equatorial and axial endocyclic Sb–O bond lengths (1.913(2) and 2.035(2) Å) vary only marginally (by 0.122(2) Å) and compare well with those of $(Ph_3SbO)_2$ (1.928(3) and 2.071(4) Å).[6] By contrast, in **6** the equatorial and axial endocyclic Te–O bond lengths (1.897(5) and 2.143(5) Å) differ by 0.246(5) Å.

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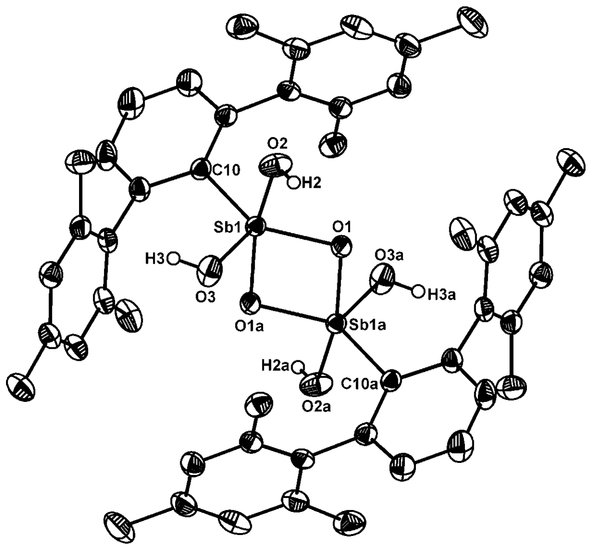

Figure 1. Molecular structure of **3**; thermal ellipsoids are set at the 30% probability level. Selected bond parameters [Å,°]: Sb1–O1 1.913(2), Sb1–O1a 2.035(2), Sb1–O2 1.940(3), Sb1–O3 1.917(3), Sb1–C10 2.136(3); O1-Sb1-O3 118.4(1), O1-Sb1-O2 91.9(1), O3-Sb1-O2 87.8(1), O1-Sb1-O1a 78.1(1), O2-Sb1-O1a 165.7(1), O3-Sb1-O1a 88.1(1), O1-Sb1-C10 125.6(1), O1a-Sb1-C10 94.9(1), O2-Sb1-C10 99.2(1), O3-Sb1-C10 115.1(1), Sb1-O1-Sb1a 102.0(1).

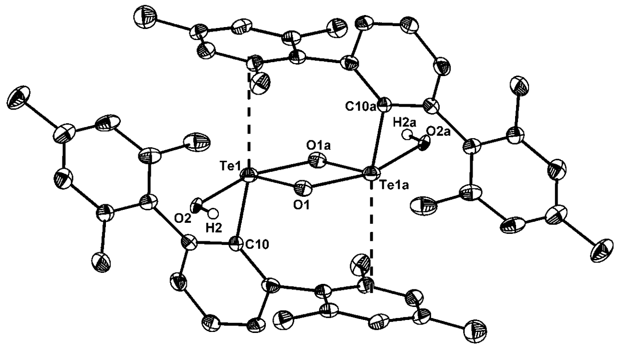

Figure 2. Molecular structure of **6**; thermal ellipsoids are set at the 30% probability level. Selected bond parameters [Å,°]: Te1–O1 1.897(5), Te1–O1a 2.143(5), Te1–O2 2.232(4), Te1–C10 2.151(6); O1-Te1-O1a 76.5(2), O1-Te1-C10 108.4(2), O1a-Te1-C10 89.3(2), O1-Te1-O2 86.0(2), O1a-Te1-O2 161.2(2), C10-Te1-O2 89.68(2), Te1-O1-Te1a 103.5(2).

In the related compound $(Ph_2TeO)_2$, the difference between the equatorial and axial Te–O bonds (av 1.89(1) and 2.55(1) Å) of 0.66(1) Å is even more pronounced. This compound can be viewed as two Ph_2TeO monomers that are only weakly associated by secondary interactions.[7] From the relative asymmetry of the endocyclic E–O bond, it can be assumed that the degree of association within these four-membered-ring structures increases in the order $(Ph_2TeO)_2 \ll$ **6** $\ll (Ph_3SbO)_2 <$ **3**.

Unlike previously described stibonic[1] and tellurinic acids,[2] compounds **3** and **6** readily dissolve in organic solvents, such as toluene, CH_2Cl_2, and ethanol, but are insoluble in hexane or aqueous NaOH. Osmometric molecular weight determinations of **3** and **6** (2.5–5.0 $g\,kg^{-1}$ toluene) at 60 °C reveal degrees of aggregation of 2.0 and 1.6, respectively, which is consistent with the dissociation energies E_D calculated below.

In an effort to estimate the dissociation energies E_D of **3** and **6**, DFT calculations[13] were performed at the B3PW91/TZ level of theory for the μ_2-oxo bridged model compounds $[PhSb(O)(OH)_2]_2$ (**3a**) and $[PhTe(O)OH]_2$ (**6a**) and compared to the hypothetical forms of lighter phenylpnictogenic acids $[PhE(O)(OH)_2]_2$ (E = As, P) and phenylchalcogenic acids $[PhE(O)OH]_2$ (E = Se, S) with similar dinuclear structures (Figures 3 and 4). As expected, the dissociation energy E_D of the phenylchalcogenic acids $[PhE(O)OH]_2$ increases when going from E = S ($-0.6\,kJ\,mol^{-1}$) to E = Se ($16.1\,kJ\,mol^{-1}$) to E = Te ($106.2\,kJ\,mol^{-1}$). While no energy minimum was found for the μ_2-oxo bridged phenylphosphonic acids $[PhP(O)(OH)_2]_2$, the dissociation energies E_D of the heavier phenylpnictogenic acids $[PhE(O)(OH)_2]_2$ also increase when going from E = As ($47.0\,kJ\,mol^{-1}$) to E = Sb ($223.6\,kJ\,mol^{-1}$). Despite the fact that $[PhAs(O)(OH)_2]_2$ and $[PhSe(O)OH]_2$ show significant E_D values, all reported arylarsonic acids and arylseleninic acids show no evidence for the formation of μ_2-oxo bridged dimeric structures. The lighter phenylpnictogenic acids $[PhE(O)(OH)_2]_2$ (E = As, P) and phenylchalcogenic acids $[PhE(O)OH]_2$ (E = Se, S) are usually involved in hydrogen-bonded networks in the solid state and in solution. Therefore, the dissociation energies E_D

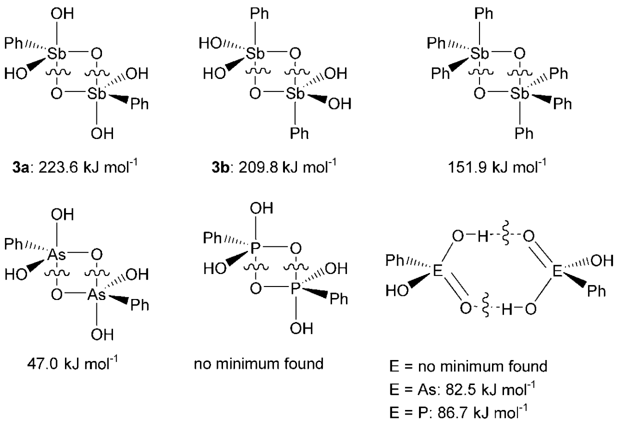

Figure 3. Dissociation energies E_D of dimeric phenylpnictogenic acids and triphenylantimony oxide.

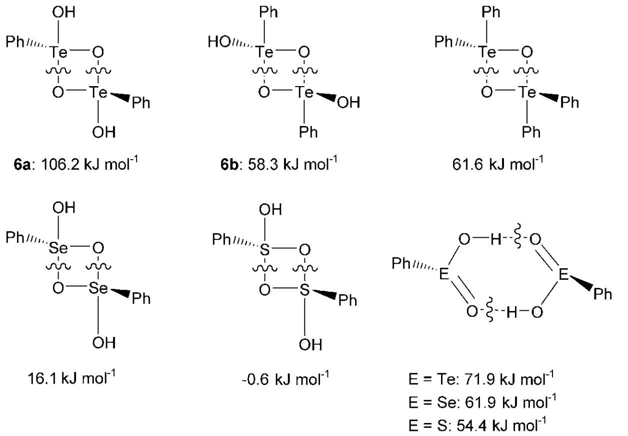

Figure 4. Dissociation energies E_D of dimeric phenylchalcogenic acids and diphenyltellurium oxide.

of two phenylpnictogenic acid molecules and two phenylchalcogenic acid molecules associated by hydrogen bonding were also calculated; these energies vary between 54.4 and 86.7 kJ mol^{-1}. The two types of aggregation for these acids might be interpreted in terms of competition between E···O=E and EOH···O=E donor–acceptor interactions. From the comparison of these E_D values it can be concluded that the μ_2-oxo-bridged dimers are energetically more favored for the heavier pnictogenic acids and chalcogenic acids of the 5th period, while for the lighter congeners of the 3rd and 4th periods the hydrogen-bonded dimers are more stable. Attempts to optimize the geometry of a hydrogen-bonded complex for $[PhSb(O)(OH)_2]_2$ gave rise to formation of a second μ_2-oxo-bridged dimer **3b**, in which the phenyl groups occupy the axial positions (Figure 3). Consistent with the Bent rule, the dissociation energy E_D of **3b** (209.8 kJ mol^{-1}) is only slightly lower than that of **3a** (223.6 kJ mol^{-1}). In comparison, the dissociation energy E_D of $(Ph_3SbO)_2$ (151.9 kJ mol^{-1}) is about 50 kJ mol^{-1} lower than that of **3a** and **3b**. Besides **6a**, for $[PhTe(O)(OH)]_2$ a second μ_2-oxo-bridged dimer **6b** was also calculated, in which the phenyl groups are situated in the axial positions. Interestingly, the dissociation energies E_D of **6a** (106.2 kJ mol^{-1}) and **6b** (58.3 kJ mol^{-1}) differ substantially, which might be attributed to the different *trans* effect imposed by the endocyclic axial ligands. The value for **6b** compares well with the dissociation energy E_D of $(Ph_2TeO)_2$ (61.6 kJ mol^{-1}).

The calculated dissociation energies E_D of the model compounds increase in the order $(Ph_2TeO)_2 \ll$ **6a** $\ll (Ph_3SbO)_2 <$ **3a**, reflecting the degree of association of the experimental four-membered-ring structures (see above).

Experimental Section

A solution of **1** (577 mg, 1.00 mmol) or **4** (547 mg, 1.00 mmol) in toluene (50 mL) was hydrolyzed by addition of aqueous NaOH (50 mL, 0.1 M for **2** and **3**; 10 mL, 0.5 M for **5** and **6**). The mixture was vigorously stirred for 1 h (for **2** and **5**) or 24 h (for **3** and **6**) before the layers were separated. The organic layer was dried over Na_2SO_4 and the solvent removed under reduced pressure to give a colorless solid.

2 (recrystallized from CH_2Cl_2/hexane): Yield 482 mg, 0.478 mmol; 96%. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.57$ (t, ^3J(H,H) = 7.5 Hz, 1H), 7.20 (d, ^3J(H,H) = 7.4 Hz, 2H), 6.95 (s, 4H), 2.26 (s, 6H), 2.21 ppm (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 140.3, 140.1, 138.4, 133.7, 132.4, 131.1, 129.0, 21.5, 21.1 ppm; IR (KBr): $\tilde{\nu}_{OH} = 3521$ cm^{-1}; elemental analysis (%) calcd for $C_{48}H_{52}Cl_2O_4Sb_2$ (1007.30): C 57.23, H 5.20; found: C 58.02, H 5.22.

3 (recrystallized from THF and dried in vacuum): Yield 425 mg, 0.438 mmol; 88%. ^1H NMR (400 MHz, C_6D_6): $\delta = 7.07$ (t, ^3J(H,H) = 7.6 Hz, 1H), 6.85 (s, 4H), 6.80 (d, ^3J(H,H) = 7.5 Hz, 2H), 2.17 (s, 6H), 2.15 (s, 12H), 0.92 ppm (s, 2H); ^{13}C NMR (100 MHz, C_6D_6): $\delta =$ 146.7, 138.2, 138.0, 137.4, 129.6, 128.4, 128.3, 127.8, 21.5, 21.2 ppm; IR (KBr): $\tilde{\nu}_{OH} = 3653$ cm^{-1}; elemental analysis (%) calcd for $C_{48}H_{54}O_6Sb_2$ (970.46): C 59.41, H 5.61; found: C 59.39, H 5.57.

5 (recrystallized from THF): Yield 420 mg, 0.426 mmol; 85%. ^1H NMR (400 MHz, C_6D_6): $\delta = 7.02$ (t, ^3J(H,H) = 7.5 Hz, 1H), 6.80 (d, ^3J(H,H) = 7.6 Hz, 2H), 6.77 (s, 4H), 2.27 (s, 6H), 2.04 ppm (s, 12H); ^{13}C NMR (100 MHz, C_6D_6): $\delta = 148.0$, 140.8, 136.4, 135.9, 128.5, 127.9, 127.6, 127.2, 20.8, 20.7 ppm; ^{125}Te NMR (126 MHz, C_6D_6): $\delta = 1372$ ppm; elemental analysis (%) calcd for $C_{48}H_{50}Cl_2O_2Te_2$ (985.02): C 58.53, H 5.12; found: C 58.24, H 4.75.

6 (recrystallized from EtOH): Yield: 441 mg, 0.465 mmol; 93% ^1H NMR (400 MHz, C_6D_6): $\delta = 7.12$ (t, ^3J(H,H) = 7.5 Hz, 1H), 6.98 (d, ^3J(H,H) = 7.5 Hz, 2H), 6.87 (s, 4H), 2.22 (s, 6H), 2.14 ppm (s, 12H); ^{13}C NMR (100 MHz, C_6D_6): $\delta = 147.6$, 140.4, 136.8, 135.5, 127.9, 127.1, 126.6, 126.2, 20.2, 19.9 ppm; ^{125}Te NMR (126 MHz, C_6D_6): $\delta = 1403$ ppm; IR (KBr): $\tilde{\nu}_{OH} = 3590$ cm^{-1}; elemental analysis (%) calcd for $C_{48}H_{52}O_4Te_2$ (948.10): C 60.81, H 5.53; found: C 60.62, H 5.14.

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[11] a) Crystal data for **3** ($C_{48}H_{54}O_6Sb_2 \cdot C_4H_8O$): $M_c = 1042.52$, monoclinic space group $P2_1/n$, $a = 11.005(2)$, $b = 9.6807(17)$, $c = 20.432(4)$ Å, $\beta = 95.673(4)°$, $V = 2166.1(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.544$ g cm^{-3}, crystal dimensions $0.38 \times 0.25 \times 0.17$ mm^3. 19846 collected and 6520 unique reflections. Final residuals $R_1 = 0.0325$, $wR_2 = 0.0802$ ($I > 2\sigma(I)$); $R_1 = 0.0454$, $wR_2 = 0.0869$ (all data). GooF = 1.093, 257 parameters; b) crystal data for **6** ($C_{48}H_{52}O_4Te_2$): $M_c = 948.12$, monoclinic space group $P2_1/n$, $a = 8.1999(14)$, $b = 16.639(3)$, $c = 15.696(3)$ Å, $\beta = 101.132(4)°$, $V = 2101.1(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.499$ g cm^{-3}, crystal dimensions $0.36 \times 0.10 \times 0.09$ mm^3. 11491 collected and 4098 unique reflections. Final residuals $R_1 = 0.0602$, $wR_2 = 0.1432$ ($I > 2\sigma(I)$); $R_1 = 0.0661$, $wR_2 = 0.1450$ (all data). GooF = 1.424, 239 parameters. CCDC-702787 (**3**) and 702790 (**6**) contain 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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[13] The calculations at the DFT/B3PW91 level of theory use the large-core correlation-consistent SDB-cc-pVTZ basis sets with the appropriate relativistic electron core potential for the heavy atoms Te and Sb and the split-valence 6-311 + G(2df,p) basis set for all other atoms. See the Supporting Information for details.