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# The First Mixed-Valent Antimony(III/V) Oxo Clusters $(2,6\text{-}Mes_2C_6H_3Sb)_2(ClSb)_4O_8$ and $(2,6\text{-}Mes_2C_6H_3Sb)_4(ClSb)_4(HOSb)_2O_{14}$[†]

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*Summary: The kinetically controlled base hydrolysis of the sterically encumbered arylantimony dichloride* $2,6\text{-}Mes_2C_6H_3\text{-}SbCl_2$ *(**1**) under aerobic conditions afforded* $[2,6\text{-}Mes_2C_6H_3\text{-}(Cl)Sb^{III}]_2O$ *(**2**) and the mixed-valent clusters* $(2,6\text{-}Mes_2C_6H_3\text{-}Sb^V)_2(ClSb^{III})_4O_8$ *(**3**) and* $(2,6\text{-}Mes_2C_6H_3Sb^V)_4(ClSb^{III})_4(HOSb^{III})_2\text{-}O_{14}$ *(**4**), whose molecular structures are dominated by hypervalent and secondary bonding.*

The first stibonic acids $RSb(O)(OH)_2$ (R = alkyl, aryl) were prepared more than 90 years ago in the context of the pharmalogical studies on arsonic acids $RAs(O)(OH)_2$, which are closely associated with the onset of modern chemotheraphy and the remedies Atoxyl and Salvarsan.[1] In sharp contrast to their lighter congeners, stibonic acids, such as $PhSb(O)(OH)_2$ and $MeSb(O)(OH)_2$,[2] are amorphous, ill-defined materials that are only poorly soluble in most solvents. These properties led to the conclusion that their structures are most likely polymeric and contain hypercoordinate antimony atoms. Notably, well-defined tri- and diorganoantimony oxides, such as $(R_3SbO)_2$ (R = Ph, *o*-$MeOC_6H_4$),[3] $(Ph_3SbO)_n$,[4] and $(R_2Sb)_4O_6$ (R = Ph, *o*-$MeC_6H_4$),[5] are also aggregated and hypercoordinate.

In an attempt to prepare a well-defined stibonic acid utilizing the stabilizing effect of a bulky organic substituent, we have studied the kinetically controlled base hydrolysis of analytically pure $2,6\text{-}Mes_2C_6H_3SbCl_2$ (**1**)[6] in a two-layer system (ether/aqueous NaOH solution) under aerobic conditions at variable reactions times (Scheme 1).[7]

After 2 h, the hydrolysis of **1** afforded the dinuclear compound $[2,6\text{-}Mes_2C_6H_3(Cl)Sb^{III}]_2O$ (**2**) as a colorless crystalline solid (Scheme 1). The molecular structure of $[2,6\text{-}Mes_2C_6H_3(Cl)Sb^{III}]_2O$ (**2**) established by single-crystal X-ray diffraction is shown in Figure 1.[8] It comprises two crystallographically independent Sb(III) sites both possessing distorted tetrahedral environments when taking into account the stereochemically active lone pair. The Sb−O bond lengths of **2** (1.947(4) and 1.966(4) Å) are comparable to those of $Me_2SbOSbMe_2$ (1.988(5) and 2.099(6) Å)[9] and $(TbtSbO)_2$ (2.004(7) and 1.990(6) Å; Tbt = $2,4,6\text{-}[(Me_3Si)_2CH]_3C_6H_2$).[10] The Sb−O−Sb angle of **2** (128.69(15)°) is also similar to that of $Me_2SbOSbMe_2$

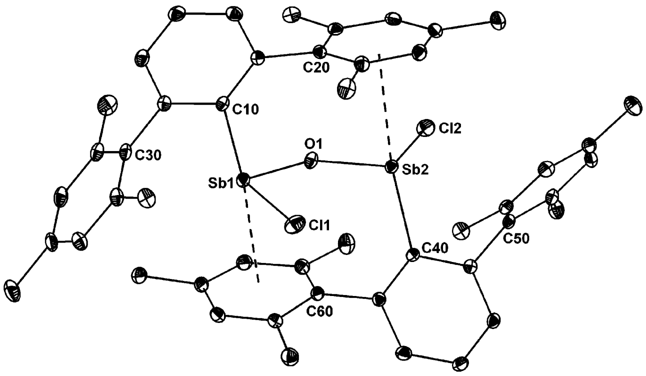
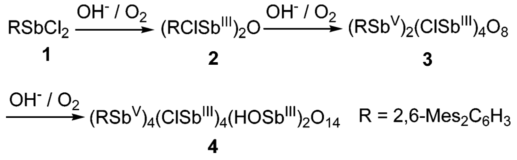


**Figure 1.** Molecular structure of $[2,6\text{-}Mes_2C_6H_3(Cl)Sb^{III}]_2O$ (**2**) showing 20% probability displacement ellipsoids and the atom numbering. Selected bond parameters [Å, deg]: Sb1−O1 1.947(4), Sb1−Cl1 2.411(6), Sb1−C10 2.188(5), Sb2−O1 1.966(4), Sb2−Cl2 2.391(4), Sb2−C40 2.189(5), O1−Sb1−Cl1 94.69(10), O1−Sb1−C10 105.2(2), Cl1−Sb1−C10 93.62(13), O1−Sb2−Cl2 93.24(18), O1−Sb2−C40 102.91(18), Cl2−Sb2−C40 94.13(19), Sb1−O1−Sb2 128.69(15).

**Scheme 1**



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[†] This work contains part of the Diploma Thesis of Timm Heek.

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(7) The starting material **1** was prepared from $2,6\text{-}Mes_2C_6H_3Li$ and $SbCl_3$ according to the literature procedure described in ref 6. An excess of $SbCl_3$ must be strictly avoided, as a crystalline adduct $\mathbf{1}\cdot SbCl_3$ may be formed. Careful control of the melting point and microanalysis allows distinguishing between pure **1** (mp 166°C; C 56.94, H 4.94) and the adduct $\mathbf{1}\cdot SbCl_3$ (mp 121°C; C 39.26, H 3.41). A solution of **1** (482 mg, 1.00 mmol) in diethyl ether (20 mL) was hydrolyzed with a solution of NaOH (30.0 mg, 0.75 mmol) in water. The mixture was vigorously stirred at room temperature in an open flask, before the reaction was stopped after 2 h (for the isolation of **2**), 10 h (for the isolation of **3**), and 20 h (for the isolation of **4**) by separating the layers. The organic layer was dried over $Na_2SO_4$, and the solvent was slowly evaporated until colorless crystals appeared. **2** (yield 71 mg, 0.074 mmol, 15%, mp 274°C): Anal. Calcd for $C_{48}H_{50}Cl_2OSb_2$ (957.28): C, 60.22; H, 5.26. Found: C, 60.33; H, 5.36. **3** (yield 96 mg, 0.060 mmol, 35%, dec 300 °C): Anal. Calcd for $C_{48}H_{50}Cl_4O_8Sb_6$ (1627.29): C, 35.43; H, 3.10. Found: C, 35.67; H, 2.74. $\mathbf{4}\cdot 2C_4H_{10}O$ (yield 45 mg, 0.015 mmol, 15 %, dec 315°C): Anal. Calcd for $C_{104}H_{122}Cl_4O_{18}\text{-}Sb_{10}$ (3019.51): C, 41.37; H, 4.07. Found: C, 41.39; H, 3.87.

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(123.0(3)°).[9] According to the VSEPR concept, the rather large Sb−O−Sb angle and the deviation from the putative tetrahedral angle are indicative of a rather high ionic bond contribution.[11]

The inorganic moiety of **2** is effectively shielded by the bulky terphenyl substitutents, while the two mesityl groups in *ortho* position are engaged in Menshutkin-type interactions with the lone pair of the Sb(III) atoms (centroid(C20−C25)···Sb2 distance 3.264(6) Å and centroid(C60−C65)···Sb1 distance 3.514(7) Å).[12] Unlike $Me_2SbOSbMe_2$,[9] no secondary Sb···X interactions (X = O, Cl) are observed between adjacent molecules.

After 10 h, the hydrolysis of **1** produced the hexanuclear cluster $(2,6\text{-}Mes_2C_6H_3Sb^{V})_2(ClSb^{III})_4O_8$ (**3**) as a colorless crystalline solid (Scheme 1). The formation of **3** can be rationalized by the hydrolytic cleavage of both Sb−Cl and Sb−C bonds within **2** and the concomitant oxidation of the remaining RSb(III) sites by air. The molecular structure of $(2,6\text{-}Mes_2C_6H_3Sb^{V})_2(ClSb^{III})_4O_8$ (**3**) established by single-crystal X-ray diffraction is shown in Figure 2.

The key feature of the structure is the dense inorganic core consisting of two organometallic Sb(V) sites and four inorganic Sb(III) atoms, which are linked by a number of primary Sb−O bonds and secondary Sb···O interactions (Figure 2b). The average $Sb^{V}$−O and $Sb^{III}$−O bond lengths, being 1.957(10) and 1.975(10) Å, respectively, differ only marginally, while the secondary $Sb^{III}$···O interactions cover a large range from 2.551(10) to 3.186(10) Å. Each Sb(III) center also binds to an exohedral Cl atom, with the average $Sb^{III}$−Cl bond length being 2.433(3) Å. Intermolecular secondary Sb···Cl contacts (Sb2A···Cl2b 3.461(11) Å, Sb2B···Cl2c 3.053(8) Å) link adjacent molecules in the crystal lattice, which is presumably the reason for the very poor solubility of **3** once it crystallized from the reaction mixture. It is worth mentioning that a recent survey has demonstrated the smooth transition of hypervalent and secondary Sb···O and Sb···Cl bonding.[13]

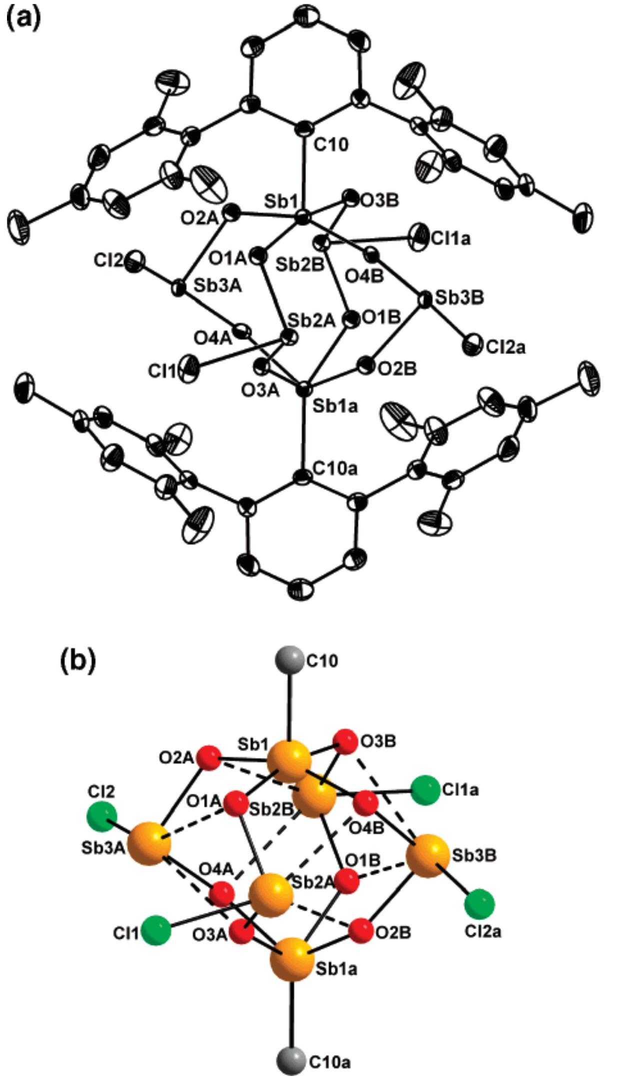

**Figure 2.** (a) Molecular structure of $(2,6\text{-}Mes_2C_6H_3Sb^{V})_2(ClSb^{III})_4O_8$ (**3**) showing 20% probability displacement ellipsoids and the atom numbering. (b) Inorganic core with primary and secondary (broken lines) contacts. Selected bond lengths [Å]: Sb1−O1A 1.966(7), Sb1−O2A 2.016(9), Sb1−O3B 1.932(7), Sb1−O4B 1.927(12), Sb1a−O1B 1.994(8), Sb1a−O2B 1.876(9), Sb1a−O3A 2.003(7), Sb1a−O4A 1.944(11), Sb1−C10 2.127(6), Sb2A−O1A 1.965(8), Sb2A−O3A 1.958(8), Sb2A−Cl1 2.461(2), Sb2B−O1B 1.998(8), Sb2B−O3B 1.965(8), Sb2B−Cl1a 2.419(2), Sb3A−O2A 2.039(9), Sb3A−O4A 1.936(12), Sb3A−Cl2 2.384(5), Sb3B−O2B 1.950(8), Sb3B−O4B 1.978(11), Sb3B−Cl2a 2.468(4) Sb2A···O2B 2.893(7), Sb2A···O4B 2.758(11), Sb2A···Cl2b 3.461(11), Sb2B···O2A 2.828(7), Sb2B···O4A 2.842(11), Sb2B···Cl2c 3.053(8), Sb3A···O1A 3.186(10), Sb3A···O3A 2.810(8), Sb3B···O1B 2.551(10), Sb3B···O3B 3.034(9).

The presence of two Sb(V) and four Sb(III) centers was independently confirmed by $^{121}Sb$ Mössbauer spectroscopy, which gives rise to two well-separated absorption peaks. The asymmetric absorption peak with small isomer shifts ($\delta$: relative to InSb) of −4.86 mm s$^{-1}$, large quadrupole coupling constant ($e^2qQ$) of 19.1 mm s$^{-1}$, and asymmetry parameter $\eta$ of 0.19 is an obvious indication of Sb(III) atoms having a stereochemically active lone pair.[14] The rather symmetric absorption with $\delta$ = 5.86, $e^2qQ$ = 8.9 mm s$^{-1}$, and $\eta$ = 0.99 falls within the range

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(8) (a) Crystal data for **2** ($C_{48}H_{50}Cl_2OSb_2$): $M_c$ = 957.28, triclinic space group $P1$, $a$ = 8.58(2) Å, $b$ = 11.95(3) Å, $c$ = 21.48(5) Å, $\alpha$ = 74.85(8)°, $\beta$ = 85.73(9)°, $\gamma$ = 83.88(8)°, $V$ = 2112(9) Å$^3$, $Z$ = 2, $\rho_{calcd}$ = 1.440 mg m$^{-3}$, crystal dimensions 0.30 × 0.20 × 0.15 mm$^3$. Of 22 669 reflections collected at 173 K, 10 295 (7974) were observed and used for all calculations. After absorption correction the structure was solved by direct methods and refined anisotropically on $F^2$. Final residuals $R_1$ = 0.0343, $wR_2$ = 0.0862 ($I > 2\sigma(I)$); $R_1$ = 0.0520, $wR_2$ = 0.0937 (all data). GooF = 1.065, 478 parameters. (b) Crystal data for **3** ($C_{48}H_{50}Cl_4O_8Sb_6$): $M_c$ = 1627.18, monoclinic space group $P2_1/n$, $a$ = 8.7910(7) Å, $b$ = 21.8251(12) Å, $c$ = 14.2469(11) Å, $\beta$ = 100.473(6)°, $V$ = 2687.9(3) Å$^3$, $Z$ = 2, $\rho_{calcd}$ = 2.010 mg m$^{-3}$, crystal dimensions 0.15 × 0.10 × 0.05 mm$^3$. Of 11 917 reflections collected at 200 K, 4712 (3751) were observed and used for all calculations. After absorption correction the structure was solved by direct methods and refined anisotropically on $F^2$. Final residuals $R_1$ = 0.0365, $wR_2$ = 0.0798 ($I > 2\sigma(I)$); $R_1$ = 0.0532, $wR_2$ = 0.0852 (all data). GooF = 1.005, 368 parameters. For details on the disordered fragments, see the Supporting Information. (c) Crystal data for $\underline{\mathbf{4}}\cdot 2C_4H_{10}O$ ($C_{104}H_{122}Cl_4O_{18}Sb_{10}$): $M_c$ = 3019.42, triclinic space group $P\bar{1}$, $a$ = 15.066(3) Å, $b$ = 15.160(3) Å, $c$ = 15.218(3) Å, $\alpha$ = 62.465(5)°, $\beta$ = 63.750(5)°, $\gamma$ = 82.683(5)°, $V$ = 2751.2(9) Å$^3$, $Z$ = 1, $\rho_{calcd}$ = 1.822 mg m$^{-3}$, crystal dimensions 0.50 × 0.25 × 0.10 mm$^3$. Of 27 579 reflections collected at 173 K, 12 462 (9353) were observed and used for all calculations. After absorption correction the structure was solved by direct methods and refined anisotropically on $F^2$. Final residuals $R_1$ = 0.0408, $wR_2$ = 0.1057 ($I > 2\sigma(I)$); $R_1$ = 0.0646, $wR_2$ = 0.1210 (all data). GooF = 1.077, 613 parameters.

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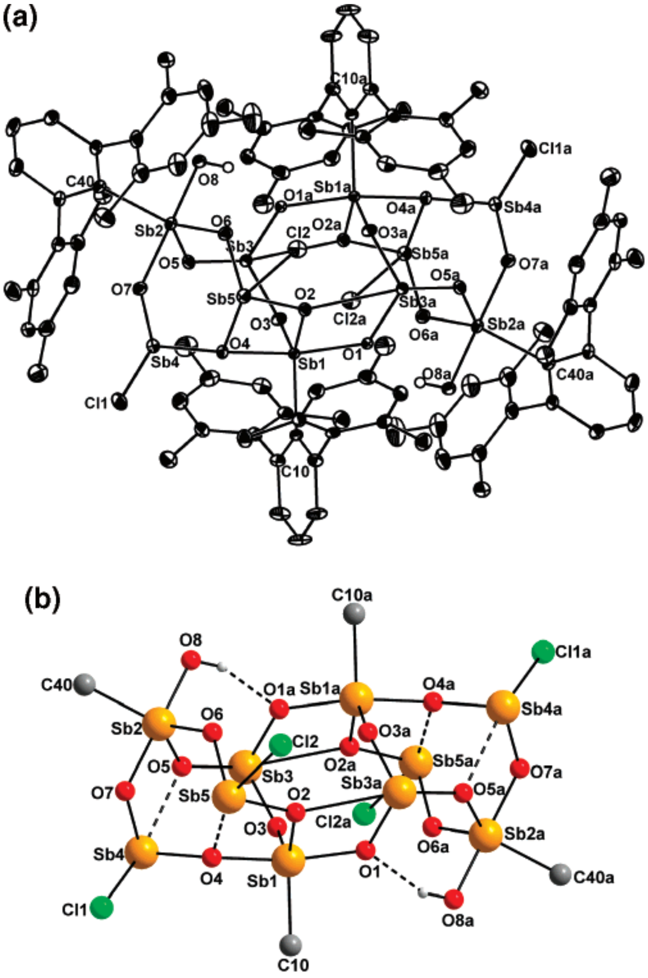

**Figure 3.** (a) Molecular structure of $(2,6\text{-}Mes_2C_6H_3Sb^{V})_4(ClSb^{III})_4(HOSb^{III})_2O_{14}$ (**4**) showing 20% probability displacement ellipsoids and the atom numbering. (b) Inorganic core with primary and secondary (broken lines) contacts. Selected bond lengths [Å]: Sb1−O1 1.973(7), Sb1−O2 1.939(10), Sb1−O3 1.890(7), Sb1−O4 2.008(7), Sb1−C10 2.146(11), Sb2−O5 1.951(7), Sb2−O6 1.914(6), Sb2−O7 1.992(8), Sb2−O8 1.935(7), Sb2−C40 2.129(10), Sb3−O1a 1.953(12), Sb3−O3 1.937(7), Sb3−O5 2.020(7), Sb4−O4 1.969(5), Sb4−O7 1.933(9), Sb4···O5 2.607(8), Sb4−Cl1 2.421(5), Sb5−O2 2.003(7), Sb5−O6 1.954(7), Sb5···O4 2.536(13), Sb5−Cl2 2.416(12).

of organoantimony(V) compounds, being close to phenylstibonic acid, $PhSb(O)(OH)_2$.[15]

After 20 h, the hydrolysis of **1** provided the dodecanuclear cluster $(2,6\text{-}Mes_2C_6H_3Sb^{V})_4(ClSb^{III})_4(HOSb^{III})_2O_{14}$ (**4**) as a colorless crystalline solid (Scheme 1). The molecular structure of **4** established by single-crystal X-ray diffraction is shown in Figure 3.[8] It comprises a centrosymmetric assembly consisting of four organometallic Sb(V) fragments and six inorganic Sb(III) sites that are linked by a number of primary Sb−O bonds and secondary Sb···O contacts. Related bond parameters are very similar to those of **3**. The formation of $(2,6\text{-}Mes_2C_6H_3Sb^{V})_4(ClSb^{III})_4(HOSb^{III})_2O_{14}$ (**4**) can be rationalized by the truncation of $(2,6\text{-}Mes_2C_6H_3Sb^{V})_2(ClSb^{III})_4O_8$ (**3**). When an OSbCl unit is formally extracted possibly initiated by a hydrolysis step, and when an exohedral chlorine atom is hydrolytically replaced by a hydroxyl group, the intermediate $(2,6\text{-}Mes_2C_6H_3Sb^{V})_2(ClSb^{III})_2(HOSb^{III})O_7$ (**3a**) is obtained, whose dimerization gives rise to **4**. The two hydroxy groups of **4** are involved in intramolecular hydrogen bonding (O8···O1a 2.767(9) Å, symmetry code $a = 1-x, -y, -z$). The hydrogen bridge is confirmed by an IR spectrum (KBr) that exhibits an OH stretching vibration at 3367 $cm^{-1}$.

In summary, we have shown that the kinetically controlled base hydrolysis of **1** under aerobic conditions provides access to novel mixed-valent multinuclear antimony(III/V) oxo clusters, such as $(2,6\text{-}Mes_2C_6H_3Sb^{V})_2(ClSb^{III})_4O_8$ (**3**) and $(2,6\text{-}Mes_2C_6H_3Sb^{V})_4(ClSb^{III})_4(HOSb^{III})_2O_{14}$ (**4**), which can be regarded as inorganic esters of (*ortho*-)stibonic acids $RSb(OH)_4$. Earlier attempts at preparing stibonic acids containing smaller organic substitutents, such as $PhSb(O)(OH)_2$, often produced amorphous ill-defined products, for which microanalyses consistently gave values that were too low in their carbon and hydrogen percentage.[2] Our results may provide a feasible explanation for this observation when assuming that similar species such as **3** and **4** had formed in the early work. Previous work on organotin oxo clusters, such as $(i\text{-}PrSn)_2(OH)_4Cl_4\cdot 2H_2O$, $(i\text{-}PrSn)_9O_8(OH)_6Cl_5\cdot 6C_2H_5SO$, $[(i\text{-}PrSn)_{12}O_{14}(OH)_6]Cl_2$, $(2,4,6\text{-}i\text{-}Pr_3C_6H_2Sn)_6O_6(OH)_6\cdot 4C_5H_{12}O$, $(2,4,6\text{-}i\text{-}Pr_3C_6H_2Sn)_8Sn_4O_{12}(OH)_{12}\cdot 12C_4H_{10}O$, $[(Me_3Si)_3CSn]_4O_6$, and $[(Me_3Si)_3C(OH)SnO]_3$, has revealed an extensive structural diversity, which depends on the method of preparation, the degree of hydrolysis, and, most importantly, the bulk of the organic substituents.[16] Efforts are underway to systematically study the influence of these parameters on the structures of organoantimony oxo clusters.

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**Note Added after ASAP Publication.** During the course of this study another mixed-valent antimony oxo cluster was reported (Kelly, B. V.; Weintrob, E. C.; Buccella, D.; Tanski, J. M.; Parkin, G. *Inorg. Chem. Commun.* **2007**, *10*, 699), namely, $\{[\kappa^4\text{-}N(CH_2(4,6\text{-}t\text{-}Bu_2C_6H_2O)_3]Sb^{V}O\}_4\{Sb_4^{III}O_6\}$, which contains four inorganic Sb(III) and Sb(V) sites.

**Supporting Information Available:** Crystallographic data of all structures as CIF files. Crystal structures of $\mathbf{1}\cdot 0.5C_4H_{10}O$ and $\mathbf{1}\cdot SbCl_3$. Details of the disordered crystal structure of **2**. Details of the Mössbauer spectrum of **2**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (excluding structure factors) have also been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-638413 (**2**), CCDC-638414 (**3**), and CCDC-638415 (**4**). 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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