

Oxidation of tetraaryldistibanes: syntheses and crystal structures of diarylantimony oxides and peroxides, $(R_2Sb)_2O$, $(R_2Sb)_4O_6$ and $(R_2SbO)_4(O_2)_2$ ($R = Ph, o\text{-Tol}, p\text{-Tol}$)

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Abstract

Tetraaryldistibanes, $(R_2Sb)_2$ ($R = Ph, o\text{-Tol}, p\text{-Tol}$) are synthesized by the reactions of R_2SbNa with $BrCH_2CH_2Br$ in liquid ammonia. They react with air oxygen to form $(R_2Sb)_2O$ and $(R_2Sb)_4O_6$. The reactions of $(R_2Sb)_4O_6$ with H_2O_2 give peroxides, $(R_2SbO)_4(O_2)_2$. Single-crystal X-ray structure analyses reveal that the conformations of the $(R_2Sb)_2O$ molecules are close to *syn-syn* ($R = Ph$) or to *syn-anti* ($R = o\text{-Tol}, p\text{-Tol}$). $(Ph_2SbO)_4(O_2)_2$ is an antimony-oxygen cluster with μ_4 -peroxo ligands. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Antimony; Oxygen; Peroxides; X-ray diffraction

1. Introduction

Tetraorganodistibanes, $(R_2Sb)_2$ ($R = \text{alkyl, aryl}$) [1] are extremely air sensitive compounds. Many alkyl derivatives ignite spontaneously when exposed to air. Tetraaryldistibanes are less reactive, but in solution they also readily absorb oxygen from the atmosphere. Reactions of distibanes with air have been studied since the 1920s and the formation of a stibinic acid $R_2Sb(O)OH$ ($R = Me$) [2] and a peroxide $R_2SbOOSbR_2$ ($R = Ph$) [3] were reported in the earlier literature. Later we used infrared and mass spectroscopy to show that the air oxidation of tetraalkyldistibanes leads to monoxides $(R_2Sb)_2O$ ($R = Me, Et, i\text{-Pr}$) [4] in the first step. It is, however, difficult to stop the oxidation of the alkyl derivatives at this stage and the products formed by complete oxidation are ill defined [2,4]. The expectation that under protection of aryl groups the stepwise oxidation might be feasible prompted our study of reactions of representative tetraaryldistibanes, $(R_2Sb)_2$ ($R = Ph, o\text{-Tol}, p\text{-Tol}$) with air and H_2O_2 and we report here the syntheses of monoxides, $(R_2Sb)_2O$, hex-

oxides, $(R_2Sb)_4O_6$, and peroxo clusters, $(R_2SbO)_4(O_2)_2$. A part of the results was already reported in a short communication [5]. $(R_2Sb)_2O$ ($R = Ph$ [1], $p\text{-Tol}$ [1]), and $(R_2Sb)_4O_6$ ($R = Ph$ [6], $o\text{-Tol}$ [7]) are known compounds, which were prepared before by other methods.

2. Results and discussion

2.1. Synthesis and oxidation of $(R_2Sb)_2$ and crystal structures of $(R_2Sb)_2O$ ($R = Ph, o\text{-Tol}, p\text{-Tol}$)

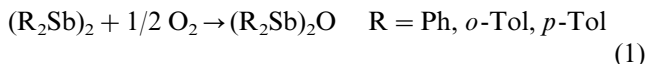
The tetraaryldistibanes, $(R_2Sb)_2$ ($R = Ph$ [8], $o\text{-Tol}$, $p\text{-Tol}$) were prepared as yellow solids by reactions of R_2SbNa with $BrCH_2CH_2Br$ and crystallization from diethylether. This method, which is well known for the synthesis of the phenyl derivative, is equally useful for the preparation of the tolyl compounds, although the yields are low. $(o\text{-Tol}_2Sb)_2$ is a novel distibane, whereas $(p\text{-Tol}_2Sb)_2$ is known for a long time as a product of the reduction of R_2SbI with sodium hypophosphite [9].

The monoxides $(R_2Sb)_2O$ ($R = Ph, o\text{-Tol}, p\text{-Tol}$) form in quantitative yields, when solutions of the distibanes in diethyl ether are exposed to the air under conditions that allow very slow absorption of oxygen. This process is easily achieved by repeatedly opening

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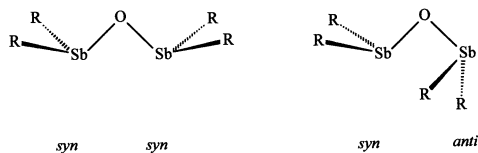
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and closing the stopper of the reaction flasks until the yellow solutions discolour.



Advantages of the oxidation (1) compared with hydrolyses of diarylantimony halides [1] are simple work-up procedures and high yields.

Interesting aspects of the structures of the $(R_2Sb)_2O$ molecules are the conformational preferences, which are described by the Ep–Sb–O–Sb torsional angles φ . Ep stands for the assumed direction of the lone pair at the antimony atoms. With assignment of the terms *syn* and *anti* for angles of 0 and 180°, the extreme conformations are *syn–syn* and *syn–anti* [10,11].



The molecular structures of $(R_2Sb)_2O$ ($R = Ph, o\text{-Tol}, p\text{-Tol}$) were determined by X-ray crystallography on single crystals obtained from diethyl ether or toluene. They are depicted in Fig. 1. Crystallographic data are presented in Table 1. Despite the close relations between these molecules their conformations are not uniform. The structure of $(Ph_2Sb)_2O$ consists of molecules in a conformation close to *syn–syn* ($\varphi_1 = 7.1^\circ$, $\varphi_2 = 43.9^\circ$), with geometric data similar to the values reported by Bordner and Andrews [12] for a sample of $(Ph_2Sb)_2O$, which presumably was obtained

by hydrolysis of Ph_2SbCl . In contrast, both tolyl compounds adopt conformations close to *syn–anti* ($o\text{-Tol}_2Sb)_2O$: $\varphi_1 = 36.0^\circ$, $\varphi_2 = 160.3^\circ$; ($p\text{-Tol}_2Sb)_2O$: $\varphi_1 = 7.4^\circ$, $\varphi_2 = 172.7^\circ$). This unspecific distribution of torsional angles φ suggests that the conformations of the molecules are almost equal in energy. For $(R_2Sb)_2O$ ($R = Ph, o\text{-Tol}, p\text{-Tol}$) the differences in energy between the various conformations are not known. Calculations for $(Me_2Sb)_2O$ revealed that the *syn–anti* conformer is only 4.6 kJ mol^{−1} higher in energy than the *syn–syn* form [10]. Almost equal amounts of both conformers are present in the gas phase [10]. In crystals of $(Me_2Sb)_2O$, however, the *syn–anti* conformation is adopted exclusively. This preference results from the association of the molecules through intermolecular Sb⋯O contacts with the formation of a $[(Me_2Sb)_2O]_x$ chain [11]. In crystals of $(R_2Sb)_2O$ ($R = Ph, o\text{-Tol}, p\text{-Tol}$) the molecules are only loosely packed to stacks without unusual contacts between them (intermolecular Sb–Sb distances $\geq 520.5(4)$ pm). Consequently the packing forces are weak and a relatively wide distribution of dihedral angles results.

The Sb–O bond lengths of $(R_2Sb)_2O$ ($R = Ph, 197.1(3), 197.8(3)$; $R = o\text{-Tol}, 196.7(2), 197.8(2)$; $R = p\text{-Tol}, 196.7(4), 198.6(4)$ pm lie in the range for single bonds not involved in intermolecular interactions, cf. $(Me_2Sb)_2O$, 198.8(5) [11]; $(RSbO)_4$ ($R = (Me_3Si)_2CH$), 196.8(3), 197.0(3) pm [13]. The Sb–O–Sb angle in the $(R_2Sb)_2O$ molecules is a little wider for the *o*-tolyl derivative ($126.5(1)^\circ$) than for the phenyl ($121.4(2)^\circ$), or *p*-tolyl ($122.2(2)^\circ$) compound. Similar values were found for $(Me_2Sb)_2O$ ($123.0(3)^\circ$) [11] and $(RSbO)_4$ ($R = (Me_3Si)_2CH$) ($122.3(2)^\circ$) [13].

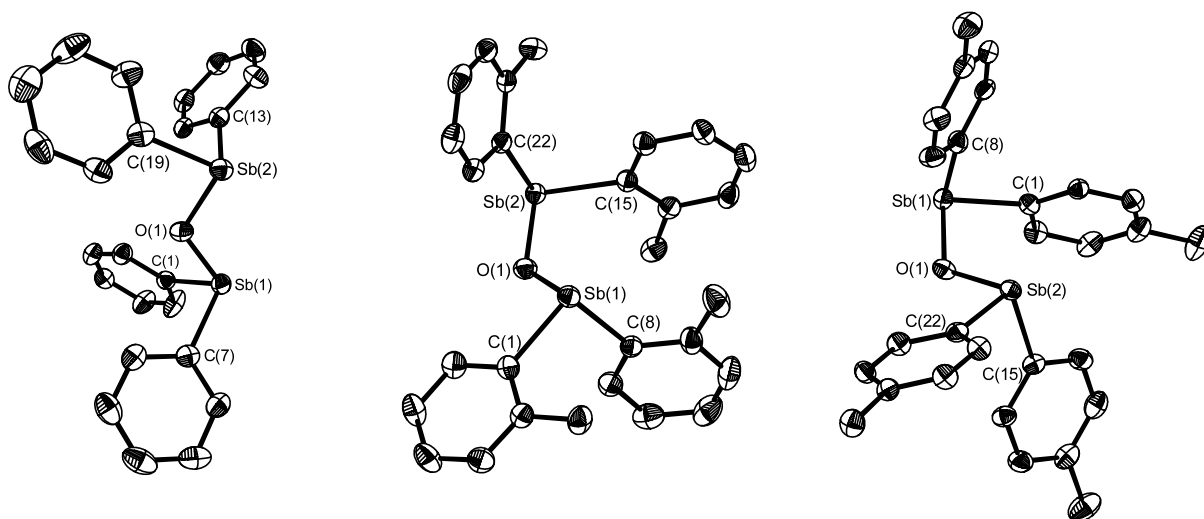


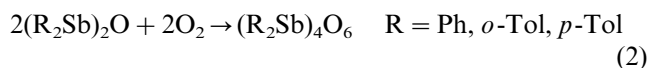
Fig. 1. Left: structure of $(Ph_2Sb)_2O$, distances (pm) and angles ($^\circ$), Sb(1)–O(1) 197.8(3), Sb(2)–O(1) 197.1(3); Sb(1)–C(1) 215.6(5), Sb(1)–C(8) 214.3(4); Sb–O–Sb 121.4(2). Centre: structure of $(o\text{-Tol}_2Sb)_2O$, Sb(1)–O(1) 197.8(2), Sb(2)–O(1) 196.7(2); Sb(1)–C(1) 215.5(3), Sb(1)–C(8) 215.4(3), Sb(2)–C(15) 216.9(3), Sb(2)–C(22) 215.0(3); Sb–O–Sb 126.5(1). Right: structure of $(p\text{-Tol}_2Sb)_2O$, Sb(1)–O(1) 196.7(4), Sb(2)–O(1) 198.6(4); Sb(1)–C(1) 213.6(5), Sb(1)–C(8) 215.0(5), Sb(2)–C(15) 215.6(5), Sb(2)–C(22) 214.6(5); Sb–O–Sb 122.2(2).

Table 1
Crystal data and structure refinement parameters

	(Ph ₂ Sb) ₂ O	(<i>o</i> -Tol ₂ Sb) ₂ O	(<i>p</i> -Tol ₂ Sb) ₂ O	(Ph ₂ SbO) ₄ (O ₂) ₂
Empirical formula	C ₂₄ H ₂₀ OSb ₂	C ₂₈ H ₂₈ OSb ₂	C ₂₈ H ₂₈ OSb ₂	C ₄₈ H ₄₀ O ₈ Sb ₄
Formula mass (g mol ⁻¹)	567.90	624.00	624.00	1231.80
Colour	Colourless	Colourless	Colourless	Colourless
Crystal size (mm)	0.6 × 0.4 × 0.4	0.6 × 0.4 × 0.4	0.7 × 0.4 × 0.4	0.5 × 0.4 × 0.4
Radiation (pm)	71.073	71.073	71.073	71.073
Temperature (K)	173(2)	173(2)	173(2)	173(2)
Crystal system	Monoclinic	Triclinic	Orthorhombic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>Pna</i> 2 ₁	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions				
<i>a</i> (pm)	591.5(1)	827.7(1)	1460.7(2)	1356.6(3)
<i>b</i> (pm)	2976.2(3)	1105.0(2)	2776.1(3)	1754.6(4)
<i>c</i> (pm)	1201.4(1)	147.8(3)	611.3(1)	1876.1(3)
α (°)	90	87.69(2)	90	90
β (°)	95.26(1)	82.37(2)	90	98.97(2)
γ (°)	90	68.85(2)	90	90
<i>V</i> (nm ³)	2.1061(5)	1.2494(4)	2.4789(6)	4.411(2)
<i>Z</i>	4	2	4	4
ρ_{calc} (g cm ⁻³)	1.791	1.659	1.672	1.855
μ (mm ⁻¹)	2.576	2.179	2.196	2.477
θ Range (°)	2.67–27.50	2.66–27.49	2.61–27.50	2.57–27.50
Reflections collected	5907	6349	6736	20 315
Independent reflections	4234 (<i>R</i> _{int} = 0.0293)	5094 (<i>R</i> _{int} = 0.0218)	3250 (<i>R</i> _{int} = 0.0382)	10 127 (<i>R</i> _{int} = 0.0364)
Parameters refined	246	287	287	543
<i>R</i> ₁	0.0337	0.0261	0.0269	0.0396
<i>wR</i> ₂	0.0776	0.0685	0.0659	0.0888
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0491, <i>wR</i> ₂ = 0.0776	<i>R</i> ₁ = 0.0307, <i>wR</i> ₂ = 0.0685	<i>R</i> ₁ = 0.0300, <i>wR</i> ₂ = 0.0659	<i>R</i> ₁ = 0.0732, <i>wR</i> ₂ = 0.0888
Largest difference peak and hole (e Å ⁻³)	1.138 and -0.686	1.035 and -0.531	0.747 and -0.660	0.806 and -0.815
Absorption correction	DIFABS [16]	DIFABS [16]	DIFABS [16]	DIFABS [16]
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Diffractometer	Siemens P4	Siemens P4	Siemens P4	Siemens P4

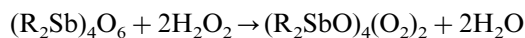
2.2. Synthesis of (R₂Sb)₄O₆ and (R₂SbO)₄(O₂)₂ (R = Ph, *o*-Tol, *p*-Tol)

Injection of a flow of air into solutions of distibanes, (R₂Sb)₂ or monoxides, (R₂Sb)₂O, in diethyl ether or other organic solvents leads to complete oxidation with precipitation of tetrakis(diarylantimony)hexoxides, (R₂Sb)₄O₆ (R = Ph, *o*-Tol, *p*-Tol). The hexoxides (stibinic acid anhydrides) are white air stable solids, insoluble in organic solvents and water.



The identity of the hexoxides was proved by elemental analyses and mass spectroscopy. Molecular ions were obtained by chemical ionization techniques. Electron impact spectra contain signals of the fragments M⁺ – R at highest mass. Attempts to grow crystals failed due to the low solubility of the compounds. Single crystals of (Ph₂Sb)₄O₆ [6] and (*o*-Tol₂Sb)₄O₆ [7] suitable for X-ray analysis were obtained from other sources and their structures were reported.

Addition of excess H₂O₂ to (R₂Sb)₄O₆ results in the formation of the peroxo clusters (R₂SbO)₄(O₂)₂ (R = Ph, *o*-Tol [5], *p*-Tol) as white crystalline solids, which in contrast to the hexoxides that are very well soluble in organic solvents. The crystals are stable for a long time. Solutions decompose after several weeks at room temperature.



Mass spectra obtained with the chemical ionization technique contain the molecular ions as the most intensive signals. The ¹H-NMR spectra show that all phenyl groups have equivalent positions. The crystal structure of (Ph₂SbO)₄(O₂)₂ was determined by X-ray structure analysis on single crystals obtained from a solution in toluene at -23 °C. The crystallographic data are given in Table 1. A view of the molecular structure is depicted in Fig. 2. The structure contains a puckered (SbO)₄ ring, where antimony atoms approximately occupy the corners of a square. Two mutually perpendicular O–O units are in capping positions above and

below the plane of the antimony atoms closing the antimony oxygen cage.

The good solubility and the relative high thermal stability of the molecules may be explained by the coordinative saturation of the atoms in the cage and by the shielding through the external phenyl groups. The O–O bond lengths of the peroxide bridges (mean 147 pm) as well as the Sb–O distances in the (SbO)₄ ring (mean 196 pm) correspond to normal single bonds. The distances between the antimony atoms and the oxygen atoms of the peroxide groups (mean 223 pm) are longer. As expected, there are only subtle differences between the structures of the phenyl- and the *o*-tolyl compound [5]. Attempts to use these compounds as sources for ¹O₂ have not yet been successful.

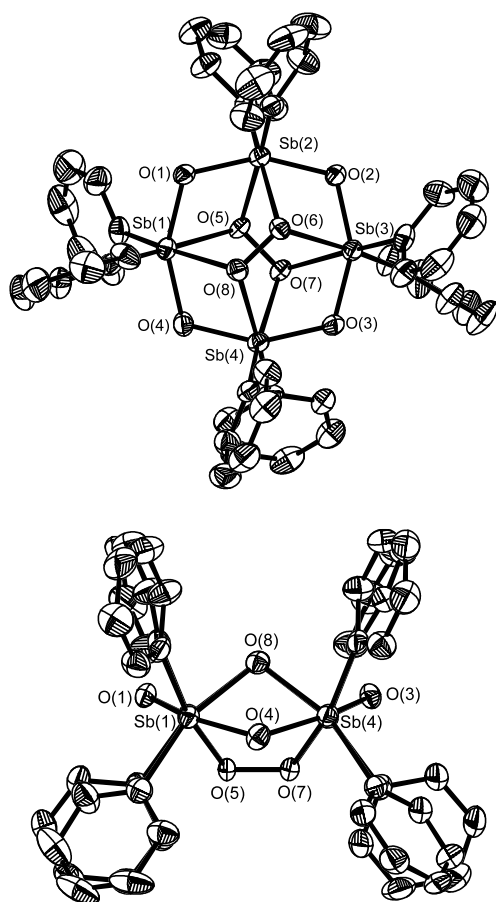


Fig. 2. Two views on the structure of (Ph₂SbO)₄(O₂)₂, (below: O(2), O(4) and O(6), O(8) are in eclipsed positions) distances (pm) and angles (°): Sb–O(O) 220.5(3)–225.1(3), Sb–C 210.3(5)–212.4(5), Sb–O(Sb) 194.6(3)–197.6(3), O(5)–O(7) 146.1(4), O(6)–O(8) 146.6(5); Sb–O(Sb)–Sb 110.89(1)–111.91(1), Sb–O(O)–Sb 92.9(1)–93.54(1), Sb–O(O)–O(O) 112.8(2)–114.2(2), O(O)–Sb–O(O) 74.51(1)–74.91(1), C–Sb–C 105.8(2)–108.1(2), O(Sb)–Sb–O(Sb) 153.96(1)–154.61(1), O(Sb)–Sb–C 92.6(2)–103.6(2), O(Sb)–Sb–O(O) 74.13(1)–75.26(1), O(O)–Sb–C 87.5(1)–91.9(2), O(Sb)–Sb–O(O) 83.95(1)–85.51(1), O(O)–Sb–C 159.6(2)–164.8(2).

3. Experimental

The experiments were performed in an Ar atmosphere, using dried solvents distilled under Ar. Ph₄Sb₂ [8], *o*-Tol₃Sb [14] and *p*-Tol₃Sb [15] were prepared as reported.

3.1. Synthesis of tetratolylidistibanes

(a) *o*-Tol₄Sb₂: 15.8 g (40 mmol) *o*-Tol₃Sb was added to a solution of 1.84 g (80 mmol) Na in 150 ml liquid NH₃ at –70 °C and the mixture was stirred for 1.5 h. The solution became dark red and 7.49 g (40 mmol) BrCH₂CH₂Br was added dropwise through a syringe. After stirring for 1 h NH₃ was allowed to evaporate. The remaining yellow solid was washed with 150 ml water, dried at reduced pressure and dissolved in 100 ml Et₂O. Cooling the yellow solution to –23 °C gave 3.46 g (28.5%) yellow crystals of *o*-Tol₄Sb₂ (m.p. 158 °C). ¹H-NMR (CDCl₃): δ = 2.48 (s, 3H, CH₃) 7.05–7.24, 7.39–7.41 (m, 4H, C₆H₄). MS (70 eV), *m/z* (%): 607 (45) [M⁺], 303 (95) [Tol₂Sb⁺], 182 (100) [Tol₂⁺]. Anal. Found: C, 55.72; H, 4.72. Calc. for C₂₈H₂₈Sb₂: C, 55.31; H, 4.64%. (b) *p*-Tol₄Sb₂: the analogous procedure with 15.8 g *p*-Tol₃Sb gave 3.82 g (31.5%) yellow *p*-Tol₄Sb₂ (m.p. 155 °C). ¹H-NMR (CDCl₃): δ = 2.36 (s, 3H, CH₃), 7.20–7.27, 7.43–7.49 (AA'XX' spin system, 4H, C₆H₄). MS (70 eV), *m/z* (%): 607 (52) [M⁺], 303 (100) [Tol₂Sb⁺], 182 (90) [Tol₂⁺]. Anal. Found: C, 54.18; H, 4.56. Calc. for C₂₈H₂₈Sb₂: C, 55.31; H, 4.64%.

3.2. Synthesis of bis(diarylantimony)oxides

(a) (Ph₂Sb)₂O: A solution of 2.00 g (3.63 mmol) Ph₄Sb₂ in 100 ml Et₂O was exposed to the air until the yellow colour of the distibane had almost disappeared. Removal of the solvent at reduced pressure gave 1.93 g (94%) (Ph₂Sb)₂O as a colourless solid. Single crystals (m.p. 78 °C, Ref. [1]: 78–81 °C) were grown from a solution in Et₂O exposed to the atmosphere at room temperature. ¹H-NMR (CDCl₃): δ = 7.40–7.45 (m, 3H, C₆H₅), 7.61–7.66 (m, 2H, C₆H₅). MS data as reported in Ref. [1]. (b) (*o*-Tol₂Sb)₂O: the analogous reaction of 2.00 g (3.29 mmol) *o*-Tol₄Sb₂ in 100 ml Et₂O gave 1.98 g (96%) of white solid (*o*-Tol₂Sb)₂O (m.p. 109 °C). Single crystals were grown in toluene at –23 °C. ¹H-NMR (CDCl₃): δ = 2.25 (s, 3H, CH₃) 7.06–7.25, 7.58–7.65 (m, 4H, C₆H₄), MS (70 eV); *m/z* (%): 624 (96) [M⁺], 533 (43) [M⁺ – Tol], 441 (10) [M⁺ – 2Tol], 303 (56), 212 (39) 181 (95), 91(100). (c) *p*-Tol₄Sb₂O: the air oxidation of 2.00 g (3.29 mmol) *p*-Tol₄Sb₂ in 100 ml Et₂O gave 2.05 g (100%) of white solid (*p*-Tol₂Sb)₂O (m.p. 101 °C, Ref. [3]: 101 °C). Single crystals were grown in toluene at –23 °C. ¹H-NMR (CDCl₃): δ = 2.33 (s, 3H, CH₃) 7.10–7.17, 7.38–7.42 (AA'XX' spin

system, 4H, C₆H₄). MS (70 eV); *m/z* (%): 624 (54) [M⁺], 533 (42), 442 (83), 394 (41), 303 (83), 212 (87), 182 (100), 91(82).

3.3. Synthesis of tetrakis(diarylantimony)hexoxides by the oxidation of distibanes

(a) (Ph₂Sb)₄O₆: 3.00 g (5.44 mmol) Ph₄Sb₂ was dissolved in 150 ml Et₂O and a gentle flow of dry air was passed through the solution until the yellow colour of the solution disappeared and the precipitation of a white solid was completed. Washing of the precipitate with Et₂O and removal of the solvent at reduced pressure gave 3.13 g (95.9%) (Ph₂Sb)₄O₆ as white solid powder (m.p. 280 °C, Ref. [6]: 285–290 °C). EIMS (280 °C, 70 eV); *m/z* (%): 1123 (2) [M⁺ – Ph], 429 (8), 352 (10), 275 (19), 198 (81), 154 (100), 77 (43) Ph; MS (DCI neg., NH₃); *m/z* (%): 1223 (100) [M[–] – Ph], 1047 (41). (b) (*o*-Tol₂Sb)₄O₆: 3.00 g (4.93 mmol) *o*-Tol₄Sb₂ reacted with air in an analogous procedure to give 3.01 g (93.0%) (*o*-Tol₂Sb)₄O₆ as a white powder (m.p. 266 °C). MS (DCI neg., NH₃) *m/z* (%): 1221 (100) [M[–] – Tol], 395 (76), 319 (25). Anal. Found: C, 51.26; H, 3.62. Calc. for C₅₆H₅₆O₆Sb₄: C, 51.26; H, 4.30%. (c) (*p*-Tol₂Sb)₄O₆: 3.00 g (4.93 mmol) *p*-Tol₄Sb₂ was reacted with air in 150 ml of Et₂O to give 3.05 g (94.4%) (*p*-Tol₂Sb)₄O₆ as white solid powder (m.p. 280 °C). MS (DCI neg., NH₃) *m/z* (%): 1221 (100) [M⁺ – Tol], 395 (28), 319 (55), 303 (5). Anal. Found: C, 50.87; H, 4.07. Calc. for C₅₆H₅₆O₆Sb₄: C, 51.26; H, 4.30%.

3.4. Synthesis of tetrakis(diarylantimony)di-μ₄-peroxo-tetroxides

(a) (Ph₂SbO)₄(O₂)₂: 100 ml of a 30% aqueous solution (0.98 mol) of H₂O₂ was added to a suspension of 3.60 g (3.0 mmol) (Ph₂Sb)₄O₆ in 100 ml Et₂O and the mixture was stirred for 4 h. Washing the precipitate with water and Et₂O and drying under reduced pressure gave 3.37 g (91.3%) (Ph₂SbO)₄(O₂)₂ as white powder (m.p. (dec.) 293 °C). Single crystals were obtained from a solution in toluene at –23 °C after 2 months. ¹H-NMR (C₆D₆): δ = 6.97–7.03 (m, 3H), 8.02–8.08 (m, 2H) MS (DCI pos., NH₃); *m/z* (%): 1233 (100) [M⁺ + H]. Anal. Found: C, 46.44; H, 3.63. Calc. for C₄₈H₄₀O₈Sb₄: C, 46.80; H, 3.27%. (b) (*o*-Tol₂Sb)₄O₆: 3.94 g (3.0 mmol) (*o*-Tol₂Sb)₄O₆ in 100 ml Et₂O and 100 ml of a 30% aqueous solution (0.98 mol) of H₂O₂ reacted to give 3.78 g (93.7%) (*o*-Tol₂SbO)₄(O₂)₂ as white powder (m.p. (dec.) 273 °C). ¹H-NMR (C₆D₆): δ = 2.45 (s, 3H), 6.75 (t, ³J = 3 Hz, 1H), 6.92 (d, ³J = 8 Hz, 1H), 7.00 (t, ³J = 3 Hz, 1H), 7.93 (d, ³J = 8 Hz, 1H). MS (DCI pos., NH₃); *m/z* (%): 1345 (100) [M⁺ + H]. Anal. Found: C, 50.39; H, 4.70. Calc. for C₅₆H₅₆O₈Sb₄: C, 50.04; H, 4.20%. (c) (*p*-

Tol₂SbO)₄(O₂)₂: 3.94 g (3.0 mmol) (*p*-Tol₂Sb)₄O₆ in 100 ml Et₂O and 100 ml of a 30% aqueous solution (0.98 mol) of H₂O₂ reacted to give 3.72 g (92.4%) (*p*-Tol₂SbO)₄(O₂)₂ as a white powder (m.p. (dec.), 281 °C). ¹H-NMR (C₆D₆): δ = 1.92 (s, 3H, CH₃), 6.8–6.9, 8.0–8.1 (m, 4H, C₆H₄). MS (DCI pos., NH₃); *m/z* (%): 1345 (100) [M⁺ + H]. Anal. Found: C, 51.02; H, 4.76. Calc. for C₅₆H₅₆O₈Sb₄: C, 50.04; H, 4.20%.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 168018, 168015–168017 for (Ph₂Sb)₂O, (*o*-Tol₂Sb)₂O, (*p*-Tol₂Sb)₂O, (Ph₂SbO)₄(O₂)₂, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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References

- [1] M. Wieber, Gmelin Handbook of Inorganic Chemistry, Sb Organoantimony Compounds, Part 2, eighth ed., Springer, Berlin, 1981.
- [2] G.T. Morgan, G.R. Davies, Proc. R. Soc. Ser. A 110 (1926) 523.
- [3] F.F. Blicke, U.O. Oakdale, F.D. Smith, J. Am. Chem. Soc. 53 (1931) 1025.
- [4] H.J. Breunig, H. Jawad, Z. Naturforsch. Teil b 37 (1982) 1104.
- [5] H.J. Breunig, T. Krüger, E. Lork, Angew. Chem. 109 (1997) 654; Angew. Chem. Int. Ed. Engl. 36 (1997) 615.
- [6] J. Bordner, G.O. Doak, T.S. Everett, J. Am. Chem. Soc. 108 (1986) 4206.
- [7] H.J. Breunig, J. Probst, K.H. Ebert, E. Lork, R. Cea-Olivares, J.-G. Alvarado-Rodriguez, Chem. Ber. Recueil 130 (1997) 959.
- [8] W. Hewertson, H.R. Watson, J. Chem. Soc. (1962) 1490.
- [9] F.F. Blicke, U.O. Oakdale, J. Am. Chem. Soc. 55 (1933) 1198.
- [10] A. Haaland, V.I. Sokolov, H.V. Volden, H.J. Breunig, M. Denker, R. Rösler, Z. Naturforsch. Teil b 52 (1997) 296.
- [11] H.J. Breunig, E. Lork, R. Rösler, G. Becker, O. Mundt, W. Schwarz, Z. Anorg. Allg. Chem. 626 (2000) 1595.
- [12] J. Bordner, B.C. Andrews, G.G. Long, Cryst. Struct. Commun. 3 (1974) 53.
- [13] H.J. Breunig, M.A. Mohammed, K.H. Ebert, Z. Naturforsch. Teil b 49 (1994) 877.
- [14] M. Benmalek, H. Chermette, C. Martelet, D. Sandino, J. Tousse, J. Organomet. Chem. 67 (1974) 53.
- [15] C. Brabant, J. Hubert, A.L. Beauchamp, Can. J. Chem. 51 (1973) 2952.
- [16] W.S. Sheldrick, Acta Crystallogr. Sect. B 32 (1976) 308.